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Effect of Aryl Substituents on the Reactivity of the Captodative Olefins 1-Acetylvinyl Arenecarboxylates

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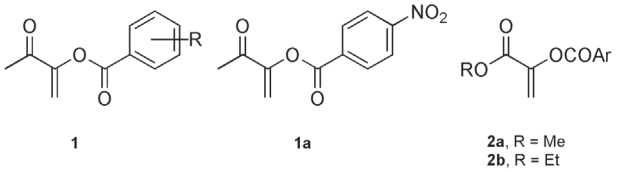
Abstract. With the aim of evaluating the effect of substitution at the aryl moiety of the aroyloxy group of captodative olefins **1** on their reactivity in Diels-Alder and other reactions, the new series of olefins 1-acetylvinyl arenecarboxylates **1c**–**1k** were prepared. No correlation was found between ^{13}C NMR chemical shifts of the carbon atoms of the double bond and the electronic effects of the diverse substituents. However, an excellent correlation was observed between the energies of the FMOs (HF/6-31G*), or the corresponding atomic coefficients or the Mülliken charges at the carbon atoms of the double bond, and the Hammett σ_m and σ_p constants of the phenyl ring substituents of some members of the series, and of some other calculated analogues. These results strongly suggest that, in addition to the major effect of the electron-withdrawing group, the reactivity of captodative olefins **1** is also controlled by the long-range inductive effects of the substituent at the phenyl ring of the aroyloxy group.
Key words: Captodative olefins, 1-acetylvinyl arenecarboxylates, FMO, Hammett constants, inductive effects.

Resumen. Con el objeto de evaluar el efecto de la sustitución del fragmento arilo del grupo aroiloxi de las olefinas captodativas **1** sobre su reactividad en reacciones de Diels-Alder y otras reacciones, se preparó la nueva serie de olefinas 1-acetilvinil arencarboxilatos **1c**–**1k**. No se encontró correlación alguna entre los desplazamientos químicos en RMN de ^{13}C de los átomos de carbono del doble enlace y los efectos electrónicos de los diversos sustituyentes. Sin embargo, se encontró una excelente correlación entre las energías de los OMF (HF/6-31G*), o los coeficientes atómicos correspondientes o las cargas de Mülliken en los átomos de carbono del doble enlace, y las constantes de Hammett σ_m y σ_p de los sustituyents del grupo fenilo de algunos miembros de la serie, y para algunos otros compuestos análogos que fueron calculados. Estos resultados sugieren fuertemente que además del efecto dominante del grupo electroatractor, la reactividad de las olefinas captodativas **1** está también controlada por el efecto inductivo a larga distancia de los sustituyentes en el fenilo del grupo aroiloxi.
Palabras clave: Olefinas captodativas, 1-acetilvinil arencarboxilatos, OMF, constantes de Hammett, efectos inductivos.

Introduction

Captodative olefins 1-acetylvinyl *p*-arenecarboxylates **1** have proved to be highly reactive and selective in Diels-Alder [1] and 1,3-dipolar cycloadditions [2], and in Friedel-Crafts reactions [3]. They are also versatile synthons and have been employed in natural product synthesis [4]. The captodative alkyl 2-aroyloxy acrylates **2a**-**2b** have shown high reactivity and selectivity in Diels-Alder reactions as well [5]. In particular, captodative olefins have attracted special interest, due to the opposite electronic demand displayed by their geminally substituted functional groups [6]. Moreover, β-substituted captodative olefins have also been prepared, showing an interesting behavior in pericyclic reactions and synthetic usefulness [7]. In this particular case, the presence of the third substituent causes a significant perturbation of the electronic properties of the double bond [8] and reduces the reactivity of these captodative olefins in Diels-Alder reactions [9].



1 **1a** **2a**, R = Me **2b**, R = Et

Structures of Compounds 1-2

The high reactivity and selectivity of captodative olefins **1** in cycloaddition reactions is rather unexpected, since the electron-releasing effect of the aroyloxy group should decrease their reactivity in comparison with a dienophile or dipolarophile bearing only an electron-withdrawing group, such as methyl vinyl ketone (**3**) [10]. Structural and theoretical studies of olefin **1a** revealed that the delocalization of the oxygen lone pair of the electron-donor group toward the π-system is inhibited by conformational preferences [11]. In addition, FMO calculations suggested a dominant effect of the acetyl electron-withdrawing group on the polarization of the double bond and explained the regioselectivity observed in Diels-Alder reactions [11]. However, the high regioselectivity shown by olefins **1** in 1,3-dipolar additions toward nitrones and nitrile oxides was better rationalized by DFT/HSAB theory [2c], which suggested that the electron-donor group plays an important role in controlling the interaction of the cycloaddends.

On the other hand, an early kinetic study of a series of alkenes **1** revealed that the presence of electron-withdrawing groups in the aryl ring of the aroyloxy substituent enhances their reactivity in Diels-Alder cycloadditions with cyclopentadiene (**4**) [12]. This observation was attributed to the inductive effect promoted by the remote substitution of the aryl ring.

Therefore, it can be inferred that the electron-donor group in these captodative olefins exerts an electronic effect significant enough to play a role on the reactivity and regiochemistry observed in both Diels-Alder and 1,3-dipolar reactions.

With the aim of evaluating the effect of the electronic and structural properties of the electron-donor (aroyloxy) group of olefins **1** on their reactivity, we hereby report the preparation and the ^{13}C NMR study of a new series of captodative olefins (**1c**–**1k**). This study was particularly focused on the effect of the electron-demand of the substituent at the phenyl ring of the aroyloxy group on the electronic properties of the captodative double bond of olefins **1**. This analysis was assisted by FMO calculations and by the investigation of the correlation between several electronic properties (atomic charges, FMO energies, and FMO atomic coefficients) with the Hammett's substituent constants.

Results and Discussion

Synthesis and ^{13}C NMR study of the new captodative olefins 1c–1k.

Although the series of substituted olefins **1** was prepared in accordance with the reported method [4b,12], by reacting diacetyl (**5**) with the corresponding aroyl chlorides **6** (Figure 1), the reaction was improved by lowering the temperature and optimizing the reaction times (Table 1). In particular, for the derivatives bearing electron-donor groups at the aryl ring, **1d**, **1e**, and **1f**, the yields increased when the reaction was carried out at -20 ºC. At a higher temperature (0 ºC) the presence of by-products complicated the purification process, reducing the yield of the desired olefin. Consequently, at the former temperature and optimal reaction times, alkenes **1a**–**1k** were obtained in satisfactory yields as pure and stable products (Table 1), which were characterized by spectroscopy and elemental analysis.

The aroyl chlorides were chosen in such a way that the type and position of the substituents at the phenyl ring allowed for the discrimination among inductive, resonance or steric effects. For example, in the case of **1a**, the nitro group at the *para* position is directly conjugated to the aroyl π-system (*-R* effect), while **1c**, has two nitro groups, which are reinforcing only the *-I* inductive effect. An analogous effect is shown by the *meta* methoxy derivative **1d**, although it induces an opposite *+R* resonance effect on the phenyl ring. In olefin **1e**, the methyl group affects the electron density of the aroyl moiety as a weak *+I* and *+R* group, while in **1f** only the *+I* effect is

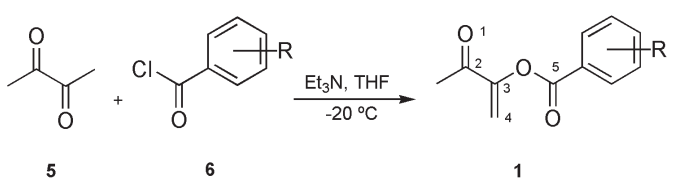


Fig. 1.

Table 1. Preparation of captodative olefins **1c**–**1k** from diacetyl (**5**) and aroyl chlorides **6**.[a]

Entry[b]	**6** [R]	t (h)	**1** (%)[c]	Mp (ºC)
1	**6c** [3,5-(NO_2)$_2$]	24	**1c** (74)	130–131
2	**6d** [3-OMe]	36	**1d** (52)	99–101
3	**6e** [4-Me]	30	**1e** (72)	173–175
4	**6f** [3-Me]	30	**1f** (70)	111–112
5	**6g** [4-Cl]	18	**1g** (71)	110–112
6	**6h** [2-Cl]	18	**1h** (58)	Oil
7	**6i** [4-Br]	24	**1i** (82)	61–62
8	**6j** [4-F]	24	**1j** (75)	67–68
9	**6k** [2-I]	20	**1k** (36)	oil

[a] For the preparation of alkene **1a** ([4-NO_2]), see ref. [4b]; for the preparation of alkene **1b** ([H]), see ref. [12]. [b] All under N_2 atmosphere, with 1.5 mol equiv. of RCOCl, 2.0 mol equiv. of Et_3N, and in THF/HMPA (94:6) as the solvent at -20 ºC. [c] After column and radial chromatography.

present. In contrast, in the *para*-substituted halogenated analogues **1g**, **1i**, and **1j**, the halogens produce a strong *-I* inductive effect along with a relatively weak *+R* effect. The proximity of an *ortho*-chloro substituent in compound **6h** might induce a strong *-I* effect on the carbonyl group, without producing a steric effect, contrary to **1k** (*ortho*-iodine), which has a weak *-I* but bulkier group.

In principle, the diverse electronic effects generated by substitution at the aryl ring should modify the polarization of the enone π-system; i.e., the electron density at the C-5 carbon atom of the carbonyl group of the aroyloxy fragment and at both C-3 and C-4 carbon atoms of the double bond (Figure 1). Therefore, an appreciable substituent effect is expected on the ^{13}C chemical shifts of these carbon atoms [13]. Table 2 summarizes the experimental chemical shifts of the captodative olefins **1a**–**1k**. In contrast with the expected effects, the ^{13}C chemical shifts of each carbon atom are very similar among the members of the series; hence no correlation can be established between the chemical shifts and the substitution pattern at the aryl ring. This is not completely surprising considering that the ^{13}C chemical shift is more responsive to resonance than it is to the inductive effect [13a].

The lack of correlation between the ^{13}C chemical shifts of the captodative double bond and substituent effects seems to be in agreement with the fact that, in the most stable conformation of the captodative olefin, the aroyloxy group in olefin **1a** is not coplanar with respect to the π orbital of the double bond, as shown by X-ray diffraction and NMR studies [11]. Hence, the resonance effects between the latter and the lone-pairs of the oxygen atom of the aroyloxy group should be inhibited. In order to further support this hypothesis, we determined the crystal structure of captodative olefin **1i** [14] (Figure 2). An almost orthogonal conformation is found between both conjugated moieties, the enone and 4-bromobenzoyloxy groups (torsion angle C2-C3-O5-C7: -62.2º), while the *s-trans* conformation of the enone is also observed. This structure is very similar to those structures of **1a** and other

Table 2. ^{13}C chemical shifts (δ, in ppm relative to TMS, in $CDCl_3$) of carbons C-3, C-4, and C-5 of captodative olefins **1a**–**1k**.

		δ		
Entry	**1** [R]	C-3	C-4	C-5
1[a]	**1a** [4-NO_2]	151.1	114.2	162.2
2[a]	**1b** [H]	151.1	113.7	164.4
3	**1c** [3,5-$(NO_2)_2$]	151.3	115.5	160.5
4	**1d** [3-OMe]	151.8	113.9	164.5
5	**1e** [4-Me]	151.9	113.4	164.5
6	**1f** [3-Me]	152.0	113.5	164.8
7	**1g** [4-Cl]	151.6	114.2	163.7
8	**1h** [2-Cl]	151.5	114.1	163.0
9	**1i** [4-Br]	151.6	114.0	163.8
10	**1j** [4-F]	151.6	113.8	163.4
11	**1k** [2-I]	151.6	114.5	164.0

[a] See ref. [12].

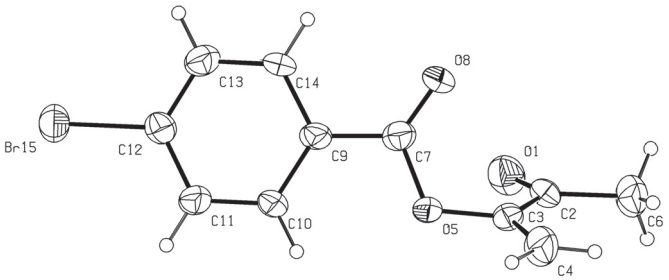


Fig. 2. X-ray structure of captodative olefin **1i** (ellipsoids with 30% probability)

analogous captodative olefins [5, 8, 9]. It is noteworthy that the length of the captodative double bond (1.277 Å) is shorter than that reported for the average values (1.34 Å) for a conjugated enone [15]. In addition, the distance (1.398 Å) between the carbon atom of the double bond and the oxygen atom of the aroyloxy group is comparable to the average value (1.353 Å) found for an unperturbed double bond formed by attaching a heteroatom at the *alpha* position [15]. This supports the idea of an insignificant resonance interaction between the lone pair of the oxygen atom of the electron donor group and the double bond, at least in the crystalline state.

Indeed, the resonance effect between the aroyloxy group and the double bond seems to be inhibited by a conformational restriction. However, the inductive effects should still be acting, since they are σ orbital-dependent. Considering that the reactivity of α,β-unsaturated alkenes in cycloaddition and Friedel-Crafts conjugate addition reactions is mostly controlled by π orbital interactions, it is likely that the reactivity of these captodative olefins is preferentially determined by the same kind of interactions. The fact that olefin **1a** is as reactive as methyl vinyl ketone (**3**) in Diels-Alder additions, and more reactive in Friedel-Crafts reactions, suggests that the conjugated carbonyl group (the electron-withdrawing group) controls

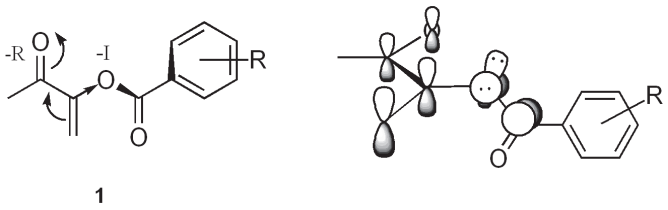


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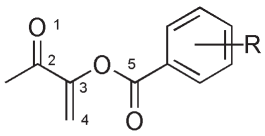
Fig. 3. Electronic effects and conformational preference of the substituents on the double bond of captodative olefins **1**.

Table 3. *Ab initio* HF/6-31G* energies (eV) of the Frontier Molecular Orbitals of olefins **1a**, **1b**, **1d**, **1e**, **1f**, **1g**, **1i**, **1j**, **1m**, **1n**, **1o**, and **1p**.[a]



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1 [R][b]	E_{HOMO}[c]	E_{LUMO}[d]	**1** [R][b]	E_{HOMO}	E_{LUMO}
1a [4-NO_2]	-11.0123	2.4580	**1i** [4-Br]	-10.7772	2.6776
1b [H]	-10.5725	2.8374	**1j** [4-F]	-10.7184	2.6379
1d [3-OMe]	-10.6387	2.8199	**1m** [3-NO_2]	-10.9295	2.5408
1e [4-Me]	-10.5725	2.8842	**1n** [4-OMe]	-10.5361	2.8618
1f [3-Me]	-10.5918	2.8597	**1o** [4-CN]	-10.9510	2.5130
1g [4-Cl]	-10.7744	2.6825	**1p** [3-CN]	-10.9108	2.5372

[a] Energies of the first FMO with significant coefficient contributions at the enone moiety. For the *meta*-substituted olefins the values shown correspond to the FMO orbitals of the most stable conformer, considering the rotation of the aryl group. [b] For the most stable non-planar *s-trans* conformation. [c] Energies of 2NHOMO. [d] Energies of the LUMO of derivative **1n**; energies of NLUMOs of derivatives **1b**, **1d**, **1e**, **1f**, **1g**, **1i**, **1j**, **1o**, and **1p**; energies of 2NLUMO of derivative **1m**.

the reactivity of these molecules. However, the aroyloxy group can also act as an activating electron-withdrawing group through a *-I* inductive effect (Figure 3). In consequence, the electronic effects of the aryl ring substituents should manifest themselves in the reactivity of these alkenes. This is supported by the relative rates of cycloadditions to cyclopentadiene among alkenes **1a**, **1b**, and **1l** (R = 2,4-$(NO_2)_2$) [12]: the more nitro groups that are present in **1** (**1l** > **1a** > **1b**), the greater the reactivity in the Diels-Alder reaction.

FMO calculations of captodative olefins and Hammett relationships.

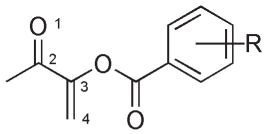
Since ^{13}C chemical shifts are not a proper index to measure these seemingly weak effects, and because of the fact that the reactions undergone by the captodative olefins are mostly controlled by MO interactions, we decided to investigate the role of the FMO energies and coefficients on the reactivity of these molecules. Tables 3 and 4 summarize the (HF/6-31G*) FMO

energies and the coefficients of the key atoms for most of the members of the prepared series of captodative olefins **1** and for olefins **1m**, **1n**, **1o**, and **1p**, which were not prepared in this study. The geometries of these olefins were fully optimized at the same level of theory, showing that the most stable geometry for all of them corresponded to the non-planar conformation of the aroyloxy group with respect to the enone moiety, and to the *s-trans* conformation of the latter. This geometry is in agreement with the X-ray structures of these molecules obtained so far, **1a** [11] and **1i** (vide supra).

As expected [16], both HOMO and LUMO are energetically stabilized when an electron-withdrawing group (NO_2 or CN) is introduced onto the aryl ring of the olefin (Table 3, **1a**, **1m**, **1o**, or **1p**), and they are destabilized in the presence of electron-donor groups, such as MeO and Me, with respect to the unsubstituted olefin **1b** (Table 3, **1d**, **1e**, **1f**, or **1n**). Interestingly, in the latter case, this effect is greater with the methoxy group, which is the strongest electron-donor group. However, in the case of halogenated olefins, it seems that there is no correlation between this effect and the electronegativity of the halogen atom. Thus, the bromine atom stabilizes both HOMO and LUMO more than the chlorine atom, and still more than the fluorine atom. This behavior might be due to a more efficient overlap between the lone-pairs orbitals of the halogen atom and the p orbitals of the ring, in the case of fluorine and chlorine atoms, which would have a stronger electron-donating effect than the bromine atom. It is worth noticing that the FMOs of the *para* chloro isomer **1g** are more stable than those of the *ortho*. This inverse correlation between distance vs. MO energy is in agreement with the expected inductive and field effects. Hence, the dominant effect is +*R* resonance over -*I* effect.

Although the contribution of the electronic effects of the substituents to the energy of the LUMOs, which are presumably the reacting orbitals of the olefins in the presence of an electron-rich diene or an aromatic ring, are in agreement with the reactivity of the captodative olefins, this is only a rough estimation of such effects. Owing to the fact that the perturbation of the substituent over the polarization and charge redistribution of the phenyl ring is due to an interplay of resonance, inductive, and electrostatic interactions, we looked for a correlation between the Hammett substituent constants, σ_m and σ_p (Table 5), which reflect the addition of all these interactions [17], and different electronic parameters such as FMO energies and Mülliken atomic charges. The *ortho* substitution was not considered due to the potential interference of steric effects. The plots of the values of the Hammett constants vs. FMO energies (HF/6-31G*) are depicted in Figures 4-5, in which one can observe a good correlation ($R^2 > 0.95$) between these two parameters. There is a decrease of energy for both HOMO and LUMO as the σ_m and σ_p values increase. Taking into account that positive values of σ indicates an electron-

Table 4. *Ab initio* HF/6-31G* p_z coefficients (C_i) of the Frontier Molecular Orbitals for olefins **1a**, **1b**, **1d**, **1e**, **1f**, **1g**, **1i**, **1j**, **1m**, **1n**, **1o**, and **1p**.[a]



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	HOMO[b]					LUMO[c]			
1 [R]	C_1	C_2	C_3	C_4	**1** [R]	C_1	C_2	C_3	C_4
1a [4-NO_2]	-0.1675	-0.0237	0.3565	0.3593	**1a** [4-NO_2]	0.2800	-0.2888	-0.2386	0.2940
1b [H]	-0.1632	-0.0227	0.3530	0.3619	**1b** [H]	0.2670	-0.2776	-0.2199	0.2681
1d [3-OMe]	-0.1640	-0.0228	0.3535	0.3621	**1d** [3-OMe]	0.2673	-0.2776	-0.2198	0.2681
1e [4-Me]	-0.1625	-0.0225	0.3526	0.3622	**1e** [4-Me]	0.2597	-0.2704	-0.2121	0.2584
1f [3-Me]	-0.1629	-0.0226	0.3527	0.3620	**1f** [3-Me]	0.2694	-0.2801	-0.2228	0.2713
1g [4-Cl]	-0.1657	-0.0233	0.3552	0.3617	**1g** [4-Cl]	0.2784	-0.2883	-0.2340	0.2863
1i [4-Br]	-0.1660	-0.0234	0.3551	0.3615	**1i** [4-Br]	0.2788	-0.2887	-0.2348	0.2873
1j [4-F]	-0.1644	-0.0229	0.3544	0.3618	**1j** [4-F]	0.2373	-0.2474	-0.1886	0.2314
1m [3-NO_2]	-0.1675	-0.0232	0.3564	0.3593	**1m** [3-NO_2]	0.2795	-0.2887	-0.2348	0.2898
1n [4-OMe]	-0.1621	-0.0224	0.3524	0.3626	**1n** [4-OMe]	0.2477	-0.2563	-0.2225	0.2690
1o [4-CN]	-0.1678	-0.0220	0.3569	0.3609	**1o** [4-CN]	0.2804	-0.2895	-0.2381	0.2928
1p [3-CN]	-0.1675	-0.0234	0.3565	0.3602	**1p** [3-CN]	0.1982	-0.2041	-0.1737	0.2137

[a] Coefficients of the FMOs of the most stable non-planar *s-trans* conformation. Only the p_z coefficients are shown, the p_z, coefficients follow a similar trend. [b] Coefficients of 2NHOMO. [c] Coefficients of the LUMOs of derivatives **1n**; energies of NLUMOs of derivatives **1b**, **1d**, **1e**, **1f**, **1g**, **1i**, **1j**, **1o**, and **1p**; energies of 2NLUMO of derivative **1m**.

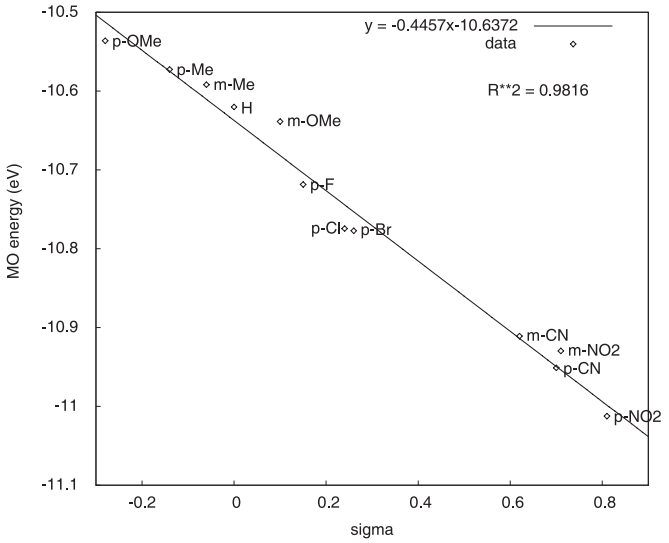


Fig. 4. Energy of the reactive HOMO vs. sigma.

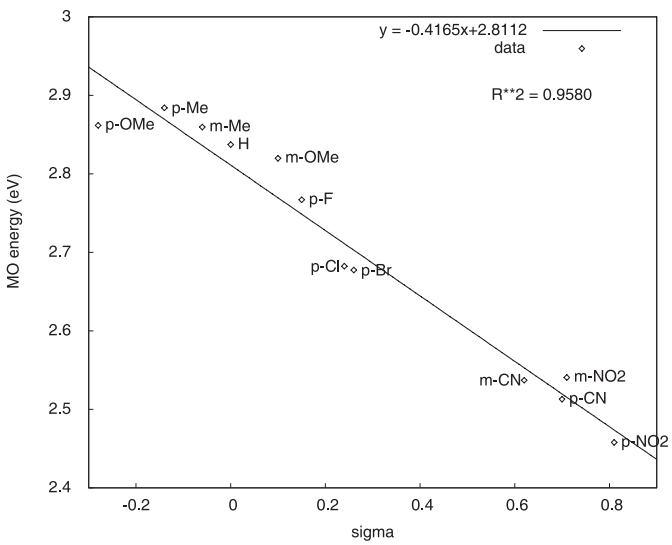


Fig. 5. Energy of the reactive LUMO vs. sigma.

withdrawing effect of the aryl ring substituent, the presence of substituents such as the nitro group increases the stabilization of the FMOs significantly. Indeed, these results support the idea that the electronic effects produced by the substitution of the aryl ring affect the polarization of the double bond of the captodative olefin.

FMO calculations indicate that captodative olefins **1** react with dienes under *normal electronic demand* in Diels-Alder cycloadditions [11, 16]. Therefore, if the stronger perturbation is given by the interaction between the HOMO of the diene and the LUMO of the dienophile, the reactivity of **1** will be enhanced with the presence of electron-withdrawing groups, such as nitro groups, as indeed is observed [12]. Although we do not have at our disposal experimental kinetic data for the olefins studied herein, the previously reported trend agrees with this observation, since those olefins bearing one or two nitro groups at the aroyloxy fragment turned out to be more reactive (about two- to four-times) than the unsubstituted one.

The Mülliken atomic charges were calculated for the series of captodative olefins **1** and they are summarized in Table 6. We found that, as expected, the carbon atoms of the carbonyl group (C-2) and of the captodative center are charge-deficient, while the oxygen atom has a negative charge. Surprisingly, the terminal unsubstituted carbon atom C-4 was not deficient, as expected for an enone moiety, but instead it was slightly electron-rich. This can explain the fact that this carbon interacts with a 1,3-dipolar species as a nucleophilic center (i.e., as a base), as borne out by the DFT/HSAB theory [2c]. Again, we found correlations between the Mülliken atomic charges and the σ_m and σ_p values (Figures 6–7). The effect of the substituent is relatively weak but the trends are significant, showing that an electron-withdrawing group such as the nitro group reduces the charge at the unsubstituted methylenic carbon (Figure 6), while an electron-donor group (Me or *p*-OMe groups) has the opposite effect. This correlation is reversed in the captodative carbon (Figure 7), probably as an effect of the polarization of the electron density of the terminal carbon atom towards the former. The regression analysis of the HOMO coefficients of the captodative and the methylenic carbons showed a trend that is in agreement with that found for the charges at these atoms (Table 4, Figures 8–9). The coefficient of the methylenic carbon becomes smaller with stronger electron-withdrawing groups (Figure 8), giving as a result a smaller contribution to the overall electron density of the carbon atom and a more positive charge. The opposite trend is found for the coefficient of the captodative carbon (Figure 9).

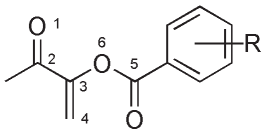
In principle, the effect of the aroyl fragment of the aroyloxy group would be reflected by the charge of the ester oxygen directly bonded to the captodative double bond. However, no clear correlation was obtained when the charges of this atom were plotted against the Hammett substituent constants. A similar observation was done when the charges of the carbonyl atom of the ester group were analyzed. However, a plot of the combined charges of the atoms of the carboxyl group did show a very good correlation with the Hammett values (Figure 10). These results seem to indicate that a change in the

Table 5. Values of the Hammett constants for the substituents at the *meta* (σ_m) or *para* (σ_p) positions of olefins **1a**, **1b**, **1d**, **1e**, **1f**, **1g**, **1i**, **1j**, **1m**, **1n**, **1o**, and **1p**.[a]

Substituent	σ_m	σ_p	Substituent	σ_m	σ_p
H	0.00	0.00	Cl	+0.37	+0.24
OMe	+0.10	-0.12	Br	+0.37	+0.26
CH_3	-0.06	-0.14	CN	+0.62	+0.70
F	+0.34	+0.15	NO_2	+0.71	+0.81

[a] Taken from ref. 17.

Table 6. *Ab initio* HF/6-31G* Mülliken charges (q) of centers 1-5, and total charge of the carboxyl group (q_{CO2}) for olefins **1a**, **1b**, **1d**, **1e**, **1f**, **1g**, **1i**, **1j**, **1m**, **1n**, **1o**, and **1p**.[a]



1

1 [R]	q_1	q_2	q_3	q_4	q_5	q_6	q_{CO_2}
1a [4-NO_2]	-0.517	0.520	0.360	-0.001	0.875	-0.681	-0.361
1b [H]	-0.516	0.518	0.368	-0.016	0.863	-0.682	-0.390
1d [3-OMe]	-0.516	0.518	0.367	-0.016	0.868	-0.682	-0.386
1e [4-Me]	-0.516	0.518	0.369	-0.019	0.864	-0.683	-0.392
1f [3-Me]	-0.516	0.518	0.369	-0.018	0.866	-0.683	-0.388
1g [4-Cl]	-0.516	0.519	0.365	-0.011	0.868	-0.683	-0.381
1i [4-Br]	-0.516	0.519	0.365	-0.010	0.869	-0.683	-0.379
1j [4-F]	-0.517	0.519	0.367	-0.013	0.870	-0.684	-0.385
1m [3-NO_2]	-0.517	0.521	0.361	-0.002	0.883	-0.682	-0.363
1n [4-OMe]	-0.516	0.518	0.371	-0.020	0.868	-0.685	-0.396
1o [4-CN]	-0.517	0.520	0.361	-0.004	0.870	-0.682	-0.369
1p [3-CN]	-0.517	0.520	0.362	-0.003	0.876	-0.683	-0.369

[a] The charge at the methylenic carbon shown here (q_4) includes the charges of the two hydrogen atoms. The actual values of the atomic charges of the carbon atom follow the same trend, although they are much more negative (about -0.44 charge units). The q_{CO_2} charge corresponds to the sum of the charges of the three atoms of the carboxyl group.

electronic effect of the aryl fragment causes a rearrangement in the electron distribution of the three atoms of the carboxyl group, and that these atoms behave as a single unit (probably because of the high conjugation) when transmitting the overall inductive effect of the aroyloxy fragment to the double bond.

Therefore, our results indicate that, in spite of the inhibition of conjugation between the lone-pairs of the oxygen atom and the π system of the enone moiety, the remote substitution at the electron-donating group of captodative olefins **1** affects the reactivity of these compounds in processes which are mainly MO-interaction dependent, such as a Diels-Alder cycloaddition. This effect is given by a change in the polarization of the charge density of the aryl ring caused by the substituent, which is mainly transmitted as far as the reactive site,

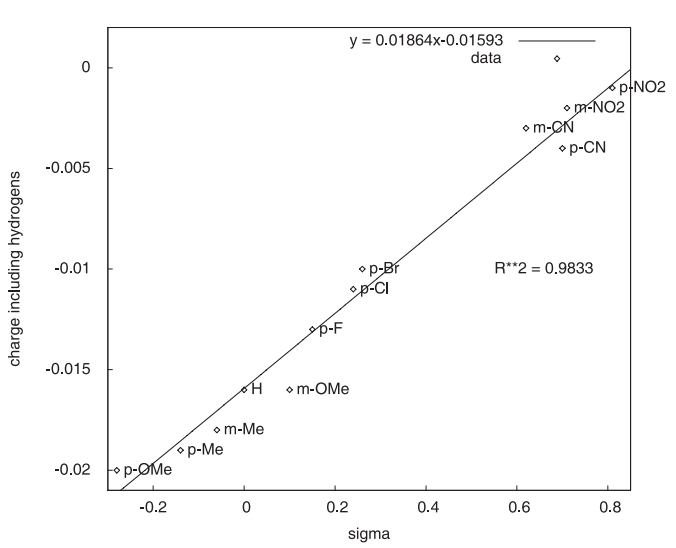


Fig. 6. Charge of the methylenic carbon (including hydrogens) vs. sigma.

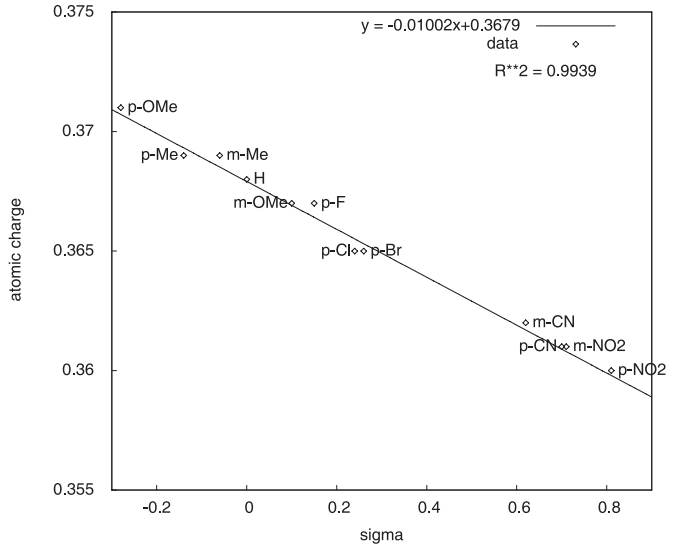


Fig. 7. Charge of the captodative carbon vs. sigma.

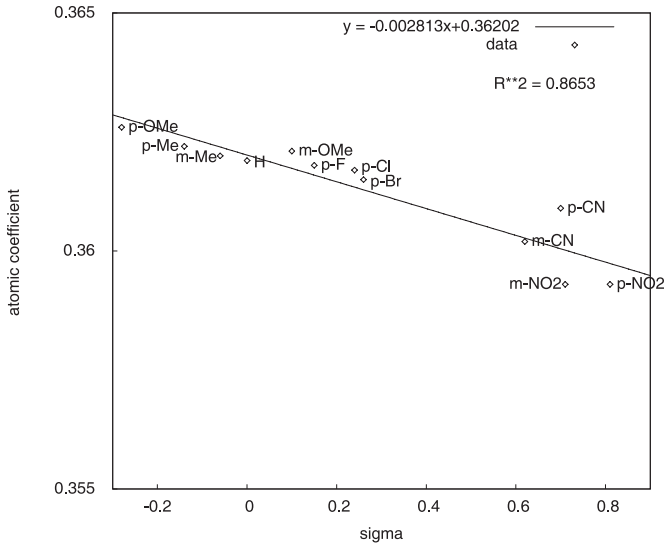


Fig. 8. HOMO coefficient of the methylenic carbon vs. sigma.

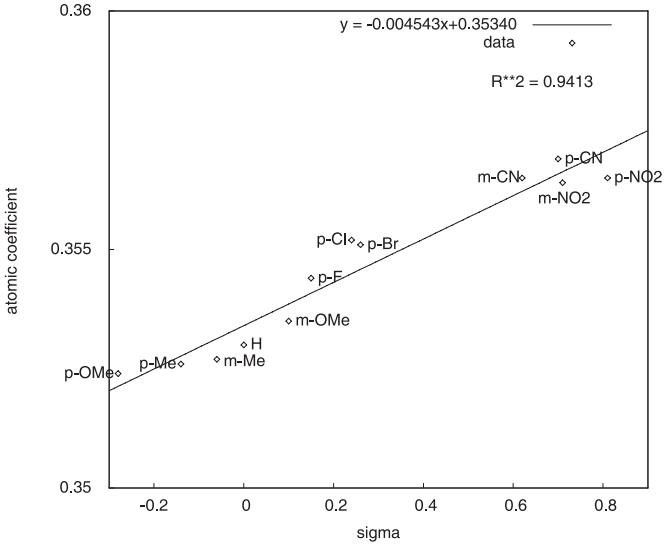


Fig. 9. HOMO coefficient of the captodative carbon vs. sigma.

the captodative double bond, by the C-O σ bond between the aroyloxy group and the enone moiety. Moreover, these results seem to account for the experimental fact that captodative olefins bearing alkoxy or silyloxy groups, as the electron-donating group, are the least reactive dienophiles in Diels-Alder cycloadditions [12]. It is likely that in the absence of the aroyloxy group, the conformational preference of the latter dienophiles be different to that observed in our captodative olefins. If conjugation between the oxygen lone pairs of the alkoxy or silyloxy groups and the double bond takes place, these groups would not be expected to exert a significant *-I* inductive effect, thus deactivating the alkene towards electrophilic attacks.

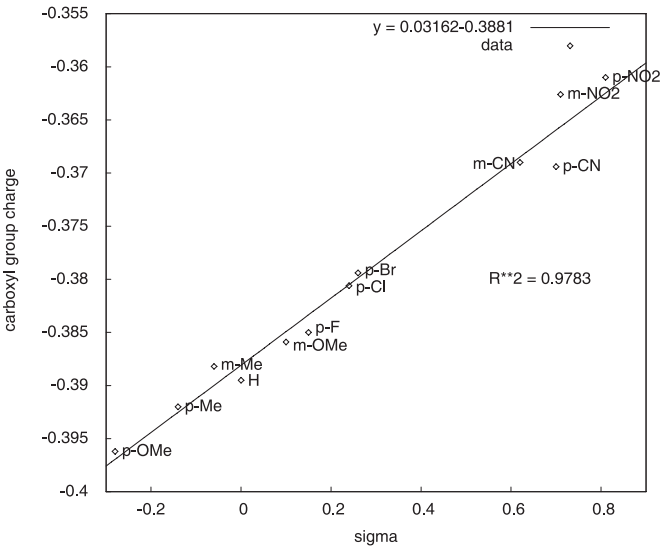


Fig. 10. Total charge of the carboxyl group vs. sigma.

Conclusions

The synthesis of the new aroyloxy substituted captodative olefins **1c**–**1k** was reported. The X-ray diffraction analysis of alkene **1i** confirmed the conformational preference of the aroyloxy group to be almost orthogonal to the plane of the enone. In this conformation, the resonance interaction between the lone-pairs of the oxygen atom with the π system of the captodative double bond is strongly inhibited. The effect of the electron-demand of the substitution pattern of the electron-donating group of these alkenes on their reactivity in concerted Diels-Alder additions was evaluated by measuring the chemical shifts of the olefinic carbon atoms in their ^{13}C NMR spectra, and by calculating FMO energies and Mülliken atom charges. Contrary to our expectation, the chemical shifts were not a reliable index for quantifying the electronic effect of the phenyl ring substituents in our captodative olefins. However, these effects were described fairly well by a correlation between the HOMO and LUMO energies or the Mülliken charges and the Hammett σ values.

In spite of the fact that we had already observed an enhancement of the reactivity of captodative olefins in Diels-Alder reactions with the presence of electron-withdrawing substituents in the aryl ring, the correlations herein found between the Hammett σ values and the LUMO energies of the captodative olefins confirm the hypothesis that, as a consequence of the conformational preference, the reactivity of these processes is not only controlled by the electron-withdrawing group of the captodative center (acetyl group), but

also by the inductive and electrostatic effects exerted by the aryl substituents of the electron-donor group of the captodative center (the aroyloxy group).

Experimental Section

General. Melting points (uncorrected) were determined with an Electrothermal capillary melting point apparatus. IR spectra were recorded on a Perkin-Elmer 1600 spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained on a Varian Gemini-300 (300 MHz and 75.4 MHz) instrument, with $CDCl_3$ as solvent and TMS as internal standard. The mass spectra (MS) were taken on a Hewlett-Packard 5971A spectrometer. X-Ray crystallographic measurements were collected on a Siemens P4 diffractometer with Mo Ka radiation (graphite crystal monochromator, λ = 0.7107 Å). Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). Analytical thin-layer chromatography was carried out using E. Merck silica gel 60 F_{254} coated 0.25 plates, visualizing by long- and short-wavelength UV lamp. All air moisture sensitive reactions were carried out under nitrogen using oven-dried glassware. THF was freshly distilled from sodium, and methylene chloride from calcium hydride, prior to use. Triethylamine was freshly distilled from NaOH. All other reagents were used without further purification. Compounds **1a** and **1b** were prepared as described previously [4b,12].

General Procedure for the Preparation of Olefins 1c–1k. Under N_2 atmosphere and vigorous magnetic stirring, a solution of 0.826 g (8.171 mmol) of triethylamine in a mixture of dry THF/HMPA (94:6) (20 mL) was cooled to -20 ºC, and a solution of the acid chloride **6** (5.31 mmol) in dry THF (15 mL) was added dropwise. At the same temperature, a solution of diacetyl (**5**) (0.351 g, 4.085 mmol) in 10 mL of dry THF was slowly added, and the temperature was allowed to increase until room temperature. The mixture was stirred for 18-36 h, the solvent was removed under vacuum, and the reaction crude was diluted with cold CH_2Cl_2 (50 mL). Then, the organic solution was successively washed with a cold 5% aqueous solution of HCl (2 × 25 mL), a cold aqueous saturated solution of NH_4Cl (2 × 25 mL), a cold 10% aqueous solution of $NaHCO_3$ (2 × 25 mL), and with a cold saturated solution of NaCl (2 × 30 mL). The organic layer was dried (Na_2SO_4), and the solvent was evaporated under vacuum. The residue was successively purified by column chromatography on silica gel treated with 10% of triethylamine (30 g/1 g of crude, hexane/EtOAc, 90:10), and by radial chromatography (hexane/CH_2Cl_2, 90:10). The solid product was dried and recrystallized from CH_2Cl_2/hexane, 6:4.

3-(3,5-Dinitrobenzoyloxy)-3-buten-2-one (1c). According to the general procedure, with 1.22 g of **6c** and after stirring for 24 h, 0.84 g (74%) of **1c** were obtained as pale brown crystals: R_f 0.20 (hexane/EtOAc, 8:2); mp 130–131 ºC; IR (CH_2Cl_2) 3048, 1748, 1696, 1630, 1541, 1349, 1142, 751 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.50 (s, 3H, CH_3CO), 5.99 (d, J = 3.0 Hz, 1H, HC=), 6.21 (d, J = 3.0 Hz, 1H, HC=), 9.21 (d, J = 2.1 Hz, 2H, Ar-H), 9.27 (t, J = 2.1 Hz, 1H, Ar-H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 25.2 (*C*H_3CO), 115.5 (C-4), 122.9 (ArCH), 129.8 (ArCH), 132.4 (ArC), 148.8 (ArC), 151.3 (C-3), 160.5 (Ar*C*O_2), 190.1 (CH_3*C*O). Anal. Calcd for $C_{11}H_8N_2O_7$: C, 47.15; H, 2.88; N, 10.00. Found: C, 47.13; H, 3.01; N, 10.06.

3-(3-Methoxybenzoyloxy)-3-buten-2-one (1d). According to the general procedure, with 0.905 g of **6d** and after stirring for 36 h, 0.47 g (52%) of **1d** were obtained as white crystals: R_f 0.50 (hexane/EtOAc, 8:2); mp 99–101 ºC; IR (CH_2Cl_2) 3018, 1733, 1697, 1601, 1586, 1489, 1466, 1431, 1283, 1216, 1183 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 3H, CH_3CO), 3.87 (s, 3H, OMe), 5.74 (d, J = 2.6 Hz, 1H, HC=), 6.04 (d, J = 2.6 Hz, 1H, HC=), 7.16 (br d, J = 8.3 Hz, 1H, Ar-H), 7.38 (dd, J = 8.3, 7.6 Hz, 1H, Ar-H), 7.61-7.63 (m, 1H, Ar-H), 7.71-7.73 (br d, J = 7.6 Hz, 1H, Ar-H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 25.5 (*C*H_3CO), 55.4 (OMe), 113.9 (C-4), 114.4 (ArCH), 120.4 (ArCH), 122.6 (ArCH), 129.5 (ArCH), 130.5 (ArC), 151.8 (C-3), 159.6 (ArC), 164.5 (Ar*C*O_2), 191.7 (CH_3*C*O); MS (70 eV) 220 (M^+, 6), 135 (100), 107 (20), 92 (11), 79 (1), 77 (15). Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.39; H, 5.45. Found: C, 65.24; H, 5.50.

3-(4-Methylbenzoyloxy)-3-buten-2-one (1e). According to the general procedure, with 0.82 g of **6e** and after stirring for 30 h, 0.6 g (72%) of **1e** were obtained as white crystals: R_f 0.22 (hexane/EtOAc, 8:2); mp 173–175 ºC; IR (CH_2Cl_2) 1790, 1735, 1698, 1611, 1423, 1178, 1123, 1084, 897 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, 3H, CH_3CO), 2.46 (s, 3H, MeAr), 5.74 (d, J = 2.2 Hz, 1H, HC=), 6.04 (d, J = 2.2 Hz, 1H, HC=), 7.27-7.34 (m, 2H, Ar-H), 7.98-8.08 (m, 2H, Ar-H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 21.6 (*C*H_3Ar), 25.5 (*C*H_3CO), 113.4 (C-4), 125.9 (ArC), 129.4 (ArCH), 130.4 (ArCH), 144.6 (ArC), 151.9 (C-3), 164.5 (Ar*C*O_2), 191.2 (CH_3*C*O); MS (70 eV) 204 (M^+, 1), 119 (100), 91 (27). Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92. Found: C, 70.70; H, 6.15.

3-(3-Methylbenzoyloxy)-3-buten-2-one (1f). According to the general procedure, with 0.82 g of **6f** and after stirring for 30 h, 0.57 g (69%) of **1f** were obtained as white crystals: R_f 0.20 (hexane/EtOAc, 8:2); mp 111–112 ºC; IR (CH_2Cl_2) 1736, 1699, 1366, 1283, 1187, 1125, 1095, 1073 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 3H, CH_3CO), 2.42 (s, 3H, MeAr), 5.72 (d, J = 2.3 Hz, 1H, HC=), 6.03 (d, J = 2.3 Hz, 1H, HC=), 7.34-7.50 (m, 2H, Ar-H), 7.91-7.98 (m, 2H, Ar-H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 21.2 (*C*H_3Ar), 25.5 (*C*H_3CO), 113.5 (C-4), 127.4 (ArCH), 128.5 (ArCH), 128.7 (ArC), 130.7 (ArCH), 134.5 (ArCH), 138.4 (ArC), 152.0 (C-3), 164.8 (Ar*C*O_2), 191.7 (CH_3*C*O). Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92. Found: C, 70.58; H, 5.88.

3-(4-Chlorobenzoyloxy)-3-buten-2-one (1g). According to the general procedure, with 0.93 g of **6g** and after stirring for 18 h, 0.92 g (71%) of **1g** were obtained as white crystals: R_f

0.52 (hexane/EtOAc, 8:2); mp 110–113 ºC; IR (CH_2Cl_2) 1737, 1700, 1594, 1487, 1418, 1245, 1124, 1091, 1013 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 3H, CH_3CO), 5.76 (d, J = 2.5 Hz, 1H, HC=), 6.05 (d, J = 2.5 Hz, 1H, HC=), 7.42-7.48 (m, 2H, Ar-H), 8.01-8.07 (m, 2H, Ar-H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 25.4 (CH_3CO), 114.2 (C-4), 127.1 (ArC), 128.9 (ArCH), 131.5 (ArCH), 140.3 (ArC), 151.6 (C-3), 163.7 ($ArCO_2$), 191.3 (CH_3CO). Anal. Calcd for $C_{11}H_9ClO_3$: C, 58.81; H, 4.04. Found: C, 58.60; H, 3.83.

3-(2-Chlorobenzoyloxy)-3-buten-2-one (1h). According to the general procedure, with 0.93 g of **6h** and after stirring for 18 h, 0.53 g (58%) of **1h** were obtained as a pale yellow oil: R_f 0.54 (hexane/EtOAc, 8:2); IR (CH_2Cl_2) 1745, 1700, 1639, 1591, 1474, 1436, 1366, 1293, 1217, 1114, 1041, 925 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, 3H, CH_3CO), 5.78 (d, J = 2.5 Hz, 1H, HC=), 6.05 (d, J = 2.5 Hz, 1H, HC=), 7.32-7.38 (m, 1H, Ar-H), 7.44-7.49 (m, 2H, ArH), 8.02-8.05 (m, 1H, Ar-H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 25.3 (CH_3CO), 114.1 (C-4), 126.6 (ArCH), 128.2 (ArC), 131.2 (ArCH), 132.1 (ArCH), 133.3 (ArCH), 134.4 (ArC), 151.5 (C-3), 163.0 ($ArCO_2$), 191.2 (CH_3CO); MS (70 eV) 224 (M^+, 1), 141 (34), 139 (100), 111 (27), 104 (2), 75 (17). Anal. Calcd for $C_{11}H_9ClO_3$: C, 58.81; H, 4.04. Found: C, 58.59; H, 4.23.

3-(4-Bromobenzoyloxy)-3-buten-2-one (1i). According to the general procedure, with 1.16 g of **6i** and after stirring for 24 h, 0.9 g (82%) of **1i** were obtained as white crystals: R_f 0.30 (hexane/EtOAc, 8:2); mp 61–62 ºC; IR (CH_2Cl_2) 1738, 1699, 1598, 1483, 1420, 1124, 1088 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 3H, CH_3CO), 5.76 (d, J = 2.5 Hz, 1H, HC=), 6.04 (d, J = 2.5 Hz, 1H, HC=), 7.60-7.65 (m, 2H, Ar-H), 7.94-7.98 (m, 2H, Ar-H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 25.4 (CH_3CO), 114.0 (C-4), 127.6 (ArC), 128.9 (ArC), 131.6 (ArCH), 131.9 (ArCH), 151.6 (C-3), 163.8 ($ArCO_2$), 191.2 (CH_3CO); MS (70 eV) 270 (M^+, 1), 268 (1), 185 (97), 183 (100), 157 (25), 155 (26), 104 (3), 76 (24). Anal. Calcd for $C_{11}H_9BrO_3$: C, 49.10; H, 3.37. Found: C, 48.95; H, 3.12.

3-(4-Fluorobenzoyloxy)-3-buten-2-one (1j). According to the general procedure, with 0.842 g of **6j** and after stirring for 24 h, 0.64 g (75%) of **1j** were obtained as white crystals: R_f 0.30 (hexane/EtOAc, 8:2); mp 67–68 ºC; IR (CH_2Cl_2) 1788, 1738, 1699, 1602, 1508, 1285, 1241, 1208, 1151, 1125, 1083, 1035, 1006 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H, CH_3CO), 5.75 (d, J = 2.4 Hz, 1H, HC=), 6.05 (d, J = 2.4 Hz, 1H, HC=), 7.12-7.18 (m, 2H, Ar-H), 8.10-8.15 (m, 2H, Ar-H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 25.2 (CH_3CO), 113.8 (C-4), 115.6 ($^2J_{CF}$ = 22.3 Hz, ArCH), 124.9 (ArC), 132.6 ($^3J_{CF}$ = 9.4 Hz, ArCH), 151.6 (C-3), 163.4 ($ArCO_2$), 166.1 ($^1J_{CF}$ = 255 Hz, ArC), 191.3 (CH_3CO); MS (70 eV) 208 (M^+, 1), 140 (10), 123 (100), 95 (37), 75 (13). Anal. Calcd for $C_{11}H_9FO_3$: C, 63.46; H, 4.36. Found: C, 63.23; H, 4.40.

3-(2-Iodobenzoyloxy)-3-buten-2-one (1k). According to the general procedure, with 1.41 g of **6k** and after stirring for 20 h, 0.46 g (36%) of **1k** were obtained as a colorless oil: R_f 0.41 (hexane/EtOAc, 8:2); IR (CH_2Cl_2) 1783, 1638, 1582, 1561, 1465, 1430, 1365, 1288, 1241, 1124, 1090, 1015 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 3H, CH_3CO), 5.81 (d, J = 2.5 Hz, 1H, HC=), 6.05 (d, J = 2.5 Hz, 1H, HC=), 7.19-7.27 (m, 1H, Ar-H), 7.43-7.49 (m, 1H, ArH), 8.04-8.06 (m, 2H, Ar-H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 25.5 (CH_3CO), 94.8 (ArC), 114.5 (C-4), 127.9 (ArCH), 131.0 (ArCH), 131.9 (ArC), 133.2 (ArCH), 141.3 (ArCH), 151.6 (C-3), 164.0 ($ArCO_2$), 191.3 (CH_3CO); MS (70 eV) 316 (M^+, 2), 231 (100), 203 (22), 190 (1), 127 (1), 104 (3), 76 (14). Anal. Calcd for $C_{11}H_9IO_3$: C, 41.80; H, 2.87. Found: C, 42.02; H, 2.90.

Single-Crystal X-Ray Crystallography [14]**.** Olefin **1i** was obtained as white crystals. These were mounted in glass fibers. Crystallographic measurements were performed on a Siemens P4 diffractometer with Mo Ka radiation (λ = 0.7107 Å; graphite monochromator) at room temperature. Two standard reflections were monitored periodically; they showed no change during data collection. Unit cell parameters were obtained from least-squares refinement of 37 reflections in the range $10.2 < 2\theta < 25.0°$. Intensities were corrected for Lorentz and polarization effects. No absorption correction was applied. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Hydrogen atoms were placed in idealized positions and their atomic coordinates refined. Unit weights were used in the refinement. The structure was solved using SHELX-97 [18], and the structure was visualized and plotted with the PLATON program package [19]. Data of **1i**: Formula: $C_{11}H_9BrO_3$: molecular weight: 269.09; cryst. syst.: orthorrombic; space group: *Pbca*; unit cell parameters: *a*, 9.1982(11), *b*, 9.5242(13), *c*, 25.078(3) (Å); α, 90, β, 90 (9), γ, 90 (deg); temp. (°K): 293 (2); Z: 8; No. of reflections collected: 3182; no. of independent reflections: 2447; no. of reflections observed: 978; data collection range: $5.5 < 2\theta < 55.02°$; *R*: 0.0870; GOF: 1.004.

Calculations. The *ab initio* SCF/HF calculations were carried out with the 6-31G* basis sets using Gaussian 94 [20]. Geometries were fully optimized at the HF/3-21G* level of theory and these were employed as starting point for optimization, at the HF/6-31G* level. In all cases the reactive HOMOs and LUMOs were located by visual inspection of the corresponding MO wavefunctions; the atomic charges, MO energies, and coefficients were extracted from the output of HF/6-31G* single point calculations on the optimized geometries employing the POP=REG Gaussian keyword.

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