Anal. Calcd for $C_{40}H_{25}F_5$: C, 79.99; H, 4.20; F, 15.81. Found: C, 79.95; H, 4.15; F, 15.96.

Reaction of HCl with 1,1-Dichloro-1-(*p*-methylphenyl)ethane (4b). In a 200-mL ampule were reacted 2.7 g (75 mmol) of HCl and 4.7 g (25 mmol) of **4b** for 4 days. After evaporation of the HCl, there remained 3.0 g of a dark blue solid. The crude product was separated by column chromatography (column and conditions as above) to yield **16b** (650 mg, 22%), **17b** (900 mg, 31%), and **20b** (1000 mg, 35%).

Reaction of HCl with 1-Chloro-1-(*p*-methylphenyl)ethylene (2b). In a 200-mL ampule were reacted 3.6 g (100 mmol) of HCl and 3.8 g (25 mmol) of **2b** for 4 days. After evaporation of the HCl, there remained 3.8 g of a dark blue solid. The crude product was separated by column chromatography (column 2.2 × 60 cm, 100 g of silica gel; solvent: 5% tetrachloromethane, 5% benzene, 90% *n*-hexane) to yield **16b** (350 mg, 12%), **17b** (400 mg, 14%), and **20b** (500 mg, 17%).

Acknowledgment. V.V.R.R. thanks the Alexander von Humboldt-Stiftung for a fellowship.

Registry No. 1a, 536-74-3; **1b**, 766-97-2; **1c**, 768-60-5; **1d**, 766-98-3; **2a**, 618-34-8; **2b**, 42107-37-9; **2d**, 83313-74-0; **4a**, 3141-41-1; **4b**, 65114-80-9; **4c**, 69151-26-4; **4d**, 66228-21-5; **15a**, 83313-75-1; **16a**, 612-71-5; **16b**, 50446-43-0; **16c**, 7509-20-8; **16d**, 448-60-2; **17a**, 83313-76-2; **17b**, 83313-77-3; **17c**, 83313-78-4; **17d**, 83313-79-5; **18a**, 10229-33-1; **19a**, 83313-80-8; **20a**, 83313-81-9; **20b**, 83313-82-0; **20c**, 83313-83-1; **20d**, 83313-84-2; HCl, 7647-01-0; 3-methyl-3-phenyl-1-indanone, 26466-19-3; 1,3,9-triphenyl-9-fluorenol, 83313-85-3; 1,3,9-triphenyl-9-chlorofluorene, 83313-86-4.

Transmission of Substituent Effects through Unsaturated Systems. 5.[1] Brønsted and Lewis Basicities of β-Substituted α,β-Unsaturated Ketones

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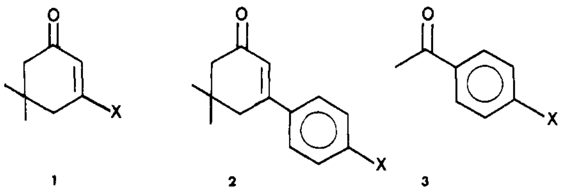
pK_{BH^+} values and enthalpies of complexation, $\Delta H°$, with boron trifluoride of a series of 16 3-substituted 5,5-dimethylcyclohex-2-en-1-ones are well correlated with σ_p^+ and σ_I,σ_R^+ constants. These compounds are therefore good models for the investigation of substituent effects on the reactivity of ethylenic systems directly substituted on the double bond. Comparisons with linear free energy relationships obtained from para-substituted 3-phenylcyclohexenones and para-substituted acetophenones allow us to evaluate the transmission factors of ethylene and phenylene groups. New σ_p^+ substituent constants are computed. Ab initio π-electron densities at the oxygen atom of the carbonyl group reproduce well the variations of Brønsted and Lewis basicities of 3-substituted cyclohexenones.

In the course of our study of substituent effects in nonaromatic systems,[2,3] we recently attempted to use the 5,5-dimethylcyclohex-2-en-1-one structure (1, Chart I) as a model compound to investigate the transmission of electronic substituent effects through a directly substituted ethylenic bond. We established the applicability of the classical substituent constants to describe some physical parameters of ground-state molecules such as ^1H and ^{13}C nuclear magnetic shielding constants[4] or infrared frequency ($\nu_{C=O}$).[5] However, some secondary effects peculiar to these spectral parameters (magnetic anisotropy effect, van der Waals steric effect, Fermi resonance and vibrational coupling effects, ...) led to only fair linear Hammett-type relationships. The next step, presented here, is to look for the applicability of Hammett-style equations to the energy differences linked to the basicity of the carbonyl function. Thus, we examine the substituent effects on pK_{BH^+} (Brønsted basicity) and the enthalpy of complex formation, $\Delta H°$ (Lewis basicity),[6] of these α-enones with boron trifluoride. This investigation may allow us (i) to test accurately the validity of mono- and multiparameter scales of substituent constants applied to this unsaturated framework, (ii) to compare the transmission factors of

Chart I



1 2 3

Scheme I

$$\text{Ketone}_{(CH_2Cl_2)} + BF_{3(gas)} \xrightarrow{\Delta H°} \text{Complex} \gt C{=}O\text{–}BF_{3(CH_2Cl_2)}$$

Scheme II

A B

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[1] Part 4: Geribaldi, S.; Azzaro, M. *Spectrochim. Acta, Part A* **1982**, *38*, 779. Also part 10 of the series "Basicity of the Carbonyl Group" (previous paper: Azzaro, M.; Gal, J. F.; Geribaldi, S.; Videau, B.; Loupy, A. *J. Chem. Soc. Perkin Trans. 2*, in press.

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Table I. pK_{BH^+} and $\Delta H°$ of 3-Substituted 5,5-Dimethylcyclohex-2-en-1-ones (at 298.15 ± 0.1 K)

compd	X	$-pK_{BH^+}$ ± 0.05[a]	$-\Delta H°$, kJ mol^{-1} [a]
1a	H	3.22	83.58 ± 0.34
b	CN	*b*	64.46 ± 0.53
c	CO_2CH_3	4.15	72.55 ± 0.57
d	Br	3.63	77.28 ± 0.18
e	Cl	3.36	77.87 ± 0.33
f	CH_2CN[c]	3.53	79.71 ± 0.26
g	$CH_2CO_2C_2H_5$	3.17	83.50 ± 0.49
h	$CH_2COC_2H_5$	3.10	85.44 ± 0.69
i	$OCOCH_3$	*b*	85.11 ± 0.35
j	$OCOC_6H_5$	*b*	83.67 ± 0.24
k	C_6H_5	2.71	86.48 ± 0.29
l	CH_3	2.50	90.56 ± 0.41
m	SC_2H_5[d]	1.43	96.64 ± 0.80
n	OCH_3	0.74	99.89 ± 0.20
o	OC_2H_5	0.69	101.25 ± 0.35
p	OH	0.45	*e*

[a] Quoted errors are for the 95% confidence level. [b] See ref 7. [c] σ_p^+ value of ref 15. [d] Substituent constants are those of SCH_3, and we keep $\sigma_R^+ = -0.85$.[14] [e] The diketonic form of 1p exists in CH_2Cl_2.

ethylenic and phenyl groups and (iii) to estimate constants for new substituents.

Results and Discussion

The pK_{BH^+} values of these weak bases 1 have been measured in aqueous sulfuric acid media. The pK_{BH^+} values obtained by using various methods[7] are in good agreement, and we shall use here the values of the Davis–Geissman method[7,8] (Table I) in order to compare them with pK_{BH^+} values of aromatic ketones[6] 2 (Chart I). Recently, we have demonstrated that the complexation enthalpy $\Delta H°$ of carbonyl compounds with boron trifluoride in methylene chloride solution (Scheme I) is a good measure of the structural effects on the Lewis basicity.[3,9] $\Delta H°$ values are reported in Table I.

The experimental stoichiometry of complex formation shows good evidence for the formation of 1:1 addition compounds apart from the cases of **1g–i**. These anomalies are attributed to the complexation (at least partial) of the carbonyl function of the substituent. Comparison of IR and ^1H NMR characteristics of free and complexed products demonstrates that the first complexation site is the carbonyl oxygen of the α-enone moiety for all the compounds.[3]

Correlations with Substituent Constants. Charton[10] has shown the equivalence of position 3 in a series of trans-3-substituted acrylic acids to the para position of benzoic acids; moreover, the resonance form B (Scheme II), valid for all electron-donating substituents X, allows us to expect through conjugation between X and the carbonyl function. At last, the substituent effect on $\Delta H°$ and pK_{BH^+} values has been expressed quantitatively for a series of para- and meta-substituted acetophenones[11,12] by $\rho^+\sigma^+$ correlations. Thus, the conjugated system 1 leads us to expect the same reactivity type and the use of σ_p^+ and σ_I,σ_R^+ constants.

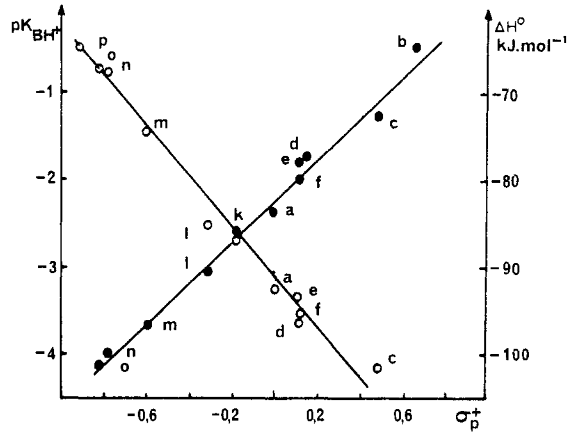

Figure 1. Plots of pK_{BH^+} (○) and $\Delta H°$ (●) vs. σ_p^+ for compounds 1.

The following relationships are obtained from all the substituents for which the substituent constants are known, except for **1g** ($X = CH_2CO_2C_2H_5$; Figure 1):

$$pK_{BH^+} = -(2.82 \pm 0.12)\sigma_p^+ - 3.10 \quad (n^{16} = 11;\ r^{16} = 0.9923;\ s^{16} = 0.18) \tag{1}$$

$$pK_{BH^+} = -(2.39 \pm 0.35)\sigma_I - (2.80 \pm 0.13)\sigma_R^+ - 3.23 \quad (n = 9;\ R^{16} = 0.9937;\ s = 0.17) \tag{2}$$

$$\Delta H° = (23.89 \pm 0.87)\sigma_p^+ - 82.05 \quad (n = 11;\ r = 0.9941;\ s = 1.34) \tag{3}$$

$$\Delta H° = (28.94 \pm 1.22)\sigma_I + (23.09 \pm 0.63)\sigma_R^+ - 83.51 \quad (n = 9;\ R = 0.9985;\ s = 0.72) \tag{4}$$

The success of these relationships definitively shows the validity of this cyclohexenonic model for investigation of the transmission of substituent effects through ethylenic systems by correlation analysis. If we compare the reaction constants ρ for the dissociation constants of *trans*-3-substituted acrylic acids and of para-substituted benzoic acids, it appears that (i) the ratio ρ(acrylic acids)/ρ(benzoic acids) is approximately 2.2 and that (ii) the resonance and polar effects operate in similar proportions in the two systems.[17,18]

Comparison of slopes in eq 1 and 2 with those obtained from pK_{BH^+} of para-substituted acetophenones 3[6] (Table II) leads to ratios $\rho^+(1)/\rho^+(3) \simeq 2.3$, $\rho_I(1)/\rho_R^+(1) \simeq 0.9$, and $\rho_I(3)/\rho_R^+(3) \simeq 1.1$. Clearly these ratios closely parallel those in carboxylic acids. This means that the reacting side chain does not affect (i) the transmitting factor of the ethylenic bond relative to the benzene ring or (ii) the ratio of inductive and resonance effects. Similar results are obtained from correlation analysis of $\Delta H°$ for series 1 and 3.[6]

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Table II. pK_{BH^+} and ΔH° of 3-(Para-substituted phenyl)cyclohexenones 2 and Para-Substituted Acetophenones (298.15 ± 0.1 K)

compd	X	$-pK_{BH^+}$[a]	$-\Delta H^\circ$, kJ mol^{-1}	compd	X	$-pK_{BH^+}$[a,b]	$-\Delta H^\circ$, kJ mol^{-1}
2a	H	2.71	86.48	**3a**	H	3.59	74.52
b	NO_2	3.20	80.28	b	NO_2	4.57	67.07
c	CN	3.09	82.20	c	CN		67.08
d	Br	2.83	84.87	d	$COCH_3$		70.58
e	Cl	2.80	85.41	e	Br	3.79	73.09
f	F	2.67	86.06	f	Cl	3.79	73.03
g	C_6H_5	2.60	87.16	g	F	3.54	
h	CH_3	2.53	88.79	h	C_6H_5		77.03
i	OCH_3	2.05	90.44	i	CH_3	3.24	77.82
				j	OCH_3	2.92	83.01

[a] The values presented here are increased 0.33 pK unit[19] compared with the pK_{BH^+} of ref 6 calculated from the too negative original H_A scale.[20] [b] For acetophenones, the pK_{BH^+} values presented are the acidity function of half-protonation, $H_A^{1/2}$ (see ref 6).

Table III. Estimated σ_p^+ Constants for a Few Substituents

substituent	σ_p^+ from 1	σ_p^+ from 3	σ_p^+ from 7
$CH_2CO_2C_2H_5$	0.02	−0.06	−0.12
$CH_2COC_2H_5$	0.00	−0.14	−0.14
$OCOCH_3$		−0.13	
$OCOC_6H_5$		−0.07	

The Brown–Okamoto equation can be applied to pK_{BH^+} and ΔH° of 3-(para-substituted phenyl)cyclohexenones **2** (Table II):[6]

$$pK_{BH^+} = -(0.69 \pm 0.04)\sigma_p^+ - 2.99 \quad (n = 9;\ r = 0.9874;\ s = 0.06) \quad (5)$$

$$\Delta H^\circ = (6.43 \pm 0.39)\sigma_p^+ - 86.01 \quad (n = 9;\ r = 0.9871;\ s = 0.53) \quad (6)$$

Comparison of the constants ρ^+ for series **1** and **2** leads to the transmission factorΠ_{Ph} of the *p*-phenylene group. We obtain 0.24 and 0.27, respectively, from pK_{BH^+} and ΔH°. These two values belong to the range of literature data for Π_{Ph} (0.25–0.40, average value 0.30).[21,22] Recently, Tsuno et al.[23] studied the transmission factor of the *p*-phenylene group using solvolysis reactions similar to those of Brown and Okamoto,[13] i.e., reactions leading to an electrophylic center.

The authors obtain $\Pi_{Ph} = 0.32$, whereas their statistic analysis of literature data leads to values between 0.31 and 0.22. Thus, the insertion of *p*-phenylene group between X and the cyclohexenone moiety does not lead to a very different attenuation compared with the attenuation observed from its insertion between X and another phenyl ring. This is attributed to a similarity of relative positions of conjugated chains which transmit substituent effects. We showed in a previous paper[1] that the average dihedral angle between the cyclohexenone and phenyl planes in structure **2** is 30°, i.e., close to the dihedral angle of biphenyl derivatives (30–35°).[23] If the angles in biphenyl derivatives and structures **2** were very different, compound **1k** (=**2a**) would show important deviations in the relationships of eq 1–4.

The excellent quality of the correlations 1–4 allows us to estimate or reestimate σ_p^+ constants for few substituents by using equations $\sigma_p^+ = (pK_{BH^+}{}^x - pK_{BH^+}{}^0)/\rho^+$ and $\sigma_p^+ = (\Delta H^\circ{}_x - \Delta H^\circ{}_0)/\rho^+$. We obtain the results reported in Table III.

Compound **1g** ($X = CH_2CO_2C_2H_5$) deviates from correlations 1 and 3. Indeed, the Brown–Okamoto $\sigma_p^+ = -0.164$ has not been calculated from the reference reaction, and it is very different from the value recently obtained by Cornish and Eaborn,[15] $\sigma_p^+ = 0.01$. Our results are in agreement with the latter value. For $X = CH_2CO_2C_2H_5$ and $CH_2COC_2H_5$, our calculated values are different according as they are estimated from pK_{BH^+} or ΔH° correlations. The relative discrepancy between these values[24] can be due to different solvations of the substituent carbonyl group in each reaction. For instance, pK_{BH^+} values are evalued in aqueous sulfuric acid solutions, and strong hydrogen bonds increase the field/inductive electron-withdrawing contribution of X (σ_p^+ increases).[25]

From eq 3 we obtain a more negative value for $\sigma_p^+(CH_2COC_2H_5)$ than for $\sigma_p^+(CH_2CO_2C_2H_5)$. This variation is in agreement with the expected effect of Y on CH_2Y. Furthermore, this decrease of σ_p^+ values when going from $Y = CO_2R$ to COR is confirmed by structural effects observed in the series $X = CH_2Y$. The literature data[22] lead to eq 7 from Y = H, CH_3, C_6H_5, OR, Cl, Br,

$$\sigma_p^+(CH_2Y) = (0.672 \pm 0.092)\sigma_I(Y) - 0.325 \quad (r = 0.9560;\ s = 0.054) \quad (7)$$

and CN, and we can estimate $\sigma_p^+(CH_2Y)$ from the σ_I constants of CO_2R and COR (Table III). Not enough data are available to achieve the same analysis for substituents OZ.

From the relationships pK_{BH^+} vs. σ_p^+ and ΔH° vs. σ_p^+ for series **1–3**, we can consider the possibility of a single extrathermodynamic relationship, pK_{BH^+} vs. ΔH°. In fact, we obtain eq 8. The existence of this relationship which

$$pK_{BH^+} = -(0.108 \pm 0.005)\Delta H^\circ - 11.97 \quad (n = 26; r = 0.9729;\ s = 0.22) \quad (8)$$

includes para-substituted acetophenones may seem surprising. Indeed, we know that cyclohexenones **1** and **2** and acetophenones **3** do not exhibit the same solvation requirements of the protonation equilibrium; i.e., protonation of **1** and **2** follows the H_A acidity function, and protonation of **3** follows a hypothetical acidity function situated between H_0 and H_A. However, the Bunnett–Olsen ϕ parameters[26] are not very different for the three model

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Table IV. Total π and σ Electron Densities at the Oxygen Atom in 3-Substituted Acroleines (Trans-s-Trans)

X	q_t	q_π	q_σ
H	6.2065	1.0984	5.1081
CN	6.1849	1.0748	5.1101
Cl	6.1930	1.0876	5.1054
CH_2CN	6.2027	1.0958	5.1069
CH_3	6.2136	1.1076	5.1060
OCH_3	6.2204	1.1220	5.0984
OH	6.2216	1.1228	5.0988

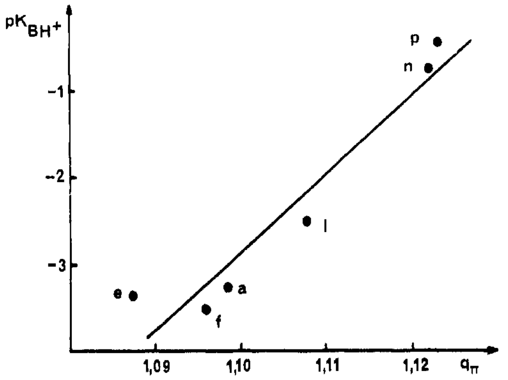

Figure 2. Correlation of pK_{BH^+} with Π-electron density for compounds 1.

compounds **1a**, **2a**, and **3a** (respectively 0.53[7], 0.55[7] and 0.44[27,28]), and this can explain the existence of eq 8. Scorrano et al.[27] have shown that delocalization of the positive charge leads to a decrease in the ϕ parameter. In fact, we observe a large decrease in ϕ on going from acetone (ϕ = 0.75)[27] to **1a**. In contrast, there is no further decrease of the ϕ value for **2a**. Thus, the α,β-enone framework is the principal contribution to the solvation that is only weakly affected by the lengthening of the conjugated system.

Correlations with Electron Densities at the Oxygen Atom. pK_{BH^+} and $\Delta H°$ are thermodynamic parameters related to equilibria in a solvating media. Therefore they should be compared with the energies of free and protonated (or complexed) bases corrected for the solvation energies.[29,30] Although, this approach is appropriate, several authors[31,32] use static indices to describe substituent effects. Among numerous reactivity indices proposed in literature,[33] electron densities at the oxygen atom of the carbonyl group seem the most suitable. Considering the large size of our compounds, we carried out ab initio calculations at the STO 3G level[34] on the model framework of 3-substituted acroleine (trans-s-trans) with standard values for bond lengths and angles[35] (Table IV).

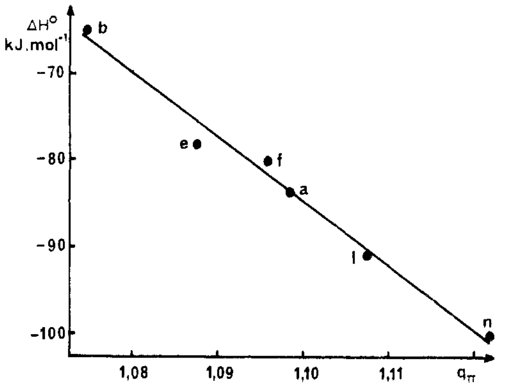

Figure 3. Correlation of $\Delta H°$ with π-electron density for compound 1.

The q_σ parameter is only weakly influenced by structural effects whereas $q\pi$ and q_t exhibit larger variations. For pK_{BH^+} as well as for $\Delta H°$, we obtain good correlations with q_t. Use of $q\pi$ gives a slightly better fit of the data than the q_t plot (Figures 2 and 3). As expected, correlations from $\Delta H°$ are better than from pK_{BH^+} (eq 9–12). Thus,

$$pK_{BH^+} = (110 \pm 28)q_t - 686.86 \quad (n = 6;\ r = 0.8886;\ s = 0.70) \quad (9)$$

$$pK_{BH^+} = (91 \pm 13)q_\pi - 102.99 \quad (n = 6;\ r = 0.9592;\ s = 0.43) \quad (10)$$

$$\Delta H° = -(896 \pm 105)q_t + 5477.14 \quad (n = 6;\ r = 0.9737;\ s = 3.06) \quad (11)$$

$$\Delta H° = -(734 \pm 48)q_\pi + 723.16 \quad (n = 6;\ r = 0.9915;\ s = 1.74) \quad (12)$$

it seems that the variations of π electron density are the source of the basicity variations in the first instance. This may be explained by the high proportion of the electrostatic component in the $>CO-H^+$ or $>CO-BF_3$ bond.[36,37]

Experimental Section

The preparation of the cyclohexenones 1 and 2 and their spectroscopic properties are described in ref 2, 4 and 38. Methods for pK_{BH^+} and $\Delta H°$ measurements have been previously reported.[7,9]

Registry No. **1a**, 4694-17-1; **1b**, 65115-71-1; **1c**, 65115-72-2; **1d**, 13271-49-3; **1e**, 17530-69-7; **1f**, 65253-25-0; **1g**, 65253-26-1; **1h**, 65253-22-7; **1i**, 18369-65-8; **1j**, 68197-30-8; **1k**, 36047-17-3; **1l**, 78-59-1; **1m**, 52735-49-6; **1n**, 4683-45-8; **1o**, 6267-39-6; **1p**, 3471-13-4; **2a**, 36047-17-3; **2b**, 29339-45-5; **2c**, 72036-56-7; **2d**, 72036-54-5; **2e**, 59344-32-0; **2f**, 72036-55-6; **2g**, 72036-53-4; **2h**, 72036-52-3; **2i**, 29339-44-4; **3a**, 98-86-2; **3b**, 100-19-6; **3c**, 1443-80-7; **3d**, 1009-61-6; **3e**, 99-90-1; **3f**, 99-91-2; **3g**, 403-42-9; **3h**, 92-91-1; **3i**, 122-00-9; **3j**, 100-06-1; BF_3, 7637-07-2.

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