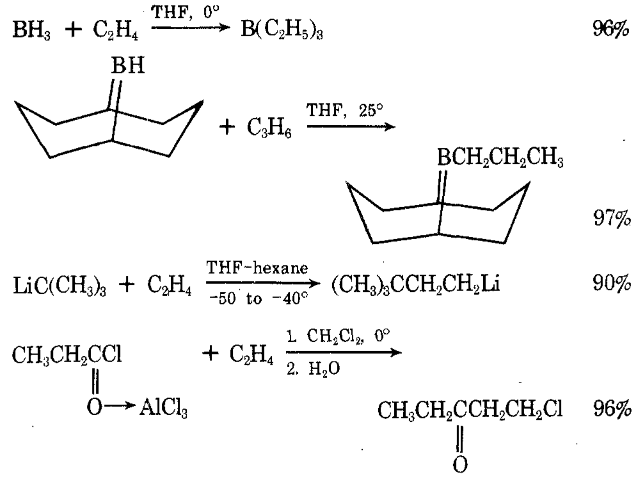
Scheme I[a]



[a] 0.95–1.05 equiv of alkene uptake in all cases.

1,2-dibromoethane and 1,2-dibromopropane, 11.6 and 9.6 *M*, respectively, proved excessive for use with common laboratory-scale reactions (10–200 mmol); 2–5 *M* solutions of the dibromoalkane in diethylene glycol or ethylcarbitol were employed.

The technique has proven useful for hydroboration,[7] anionic addition of organolithium,[8] and aliphatic acylation,[9] as shown in Scheme I. The last reaction has particular potential, as β-chloroethyl ketones are precursors of two versatile synthetic intermediates—isomerically pure vinyl ketones and Mannich bases of methyl ketones.[10]

Experimental Section

Ethylene (General Procedure). A 5 *M* solution of 1,2-dibromoethane (dried over $CaCl_2$, 94.0 g, 43.1 ml, per 100 ml solution) in diethylene glycol or similar solvent was placed in the buret. The 250-ml generator flask was charged with 35–40 g of technical zinc *powder* and 100 ml of ethylene glycol. The mixture in the generator was aggitated with a magnetic stirrer and heated to 90–100°. The apparatus was purged with dry nitrogen and the reaction mixture was introduced into the reactor. Then 0.5 ml of 1,2-dibromoethane was added to the generator. When gas evolution was observed at the bubbler, 8–9 ml of *neat* 1,2-dibromoethane was added to maintain vigorous gas evolution, purging the reactor with ethylene (~2.5 l. is produced). Upon cessation of gas evolution, stirring was begun in the reactor; the stirring rate was adjusted so that ethylene uptake did not exceed 7.5 mmol/min.

A parallel procedure was used to generate propylene from 1,2-dibromopropane. With 5.0 *M* dibromide solution, 20.5–21 ml produced 100 mmol of alkene.

***B*-Ethyl-9-borabicyclo[3.3.1]nonane.** A 125-ml reaction flask (magnetic stirring bar, injection port sealed with a rubber septum) was attached to the gas generator and purged with dry nitrogen. Into the flask was placed 56 ml (25.0 mmol) of 0.44 *M* 9-borabicyclo[3.3.1]nonane (9-BBN) in THF.[11a] The flask was placed in a 20° water bath and purged with ethylene; reaction was initiated by slowly bringing the stirrer up to the desired speed. After an initial surge saturating the solution with ethylene (0.09 mmol of C_2H_4/ml of solution) absorption continued until 25.0 mmol of ethylene had been consumed in 1.0 hr. Prolonged further stirring had no effect. Hydrolysis of a sample of the reaction mixture with THF–methanol showed no active hydride remaining.[11b] Oxidation of the reaction mixture at 0° with $NaOH-H_2O_2$[12] produced 24.3 mmol of ethanol by GLC (decane standard, UCON Polar liquid phase), a yield of 97% based on B–H or on ethylene.

***B*-*n*-Propyl-9-borabicyclo[3.3.1]nonane.** In the manner described for the *B*-ethyl compound, 9-BBN was reacted with propylene. The solution dissolves 0.55 mmol of propylene/ml. The reaction was complete in 1.0 hr, absorbing 26.1 mmol of propylene. The yield was 97% based on B–H, 93% based on propylene.

1-Chloro-3-pentanone. The 1:1 complex of propionyl chloride with aluminum chloride was ethenated in dichloromethane (2.0 *M* concentration) at 0° as described by McMahon et al.[10c] After 60 min (104 mmol of C_2H_4 used) the reaction mixture was hydrolyzed with 6.5 molar equiv of water and the $AlCl_3 \cdot 6H_2O$ sand was separated. GLC of the filtrate (decane standard, polyester column) showed 96% yield of 1-chloro-3-pentanone.

Neohexyllithium. *tert*-Butyllithium was ethenated at −40 to −50° in pentane–THF as described by Bartlett et al.[8] in 90% yield, based on reaction of the product with methyl borate and then oxidation to neohexyl alcohol.[13]

Registry No.—1,2-Dibromoethane, 106-93-4; ethylene, 74-85-1; propylene, 115-07-1; *B*-ethyl-9-borabicyclo[3.3.1]nonane, 52102-17-7; 9-borabicyclo[3.3.1]nonane, 280-64-8; *B*-*n*-propyl-9-borabicyclo[3.3.1]nonane, 1127-78-2; 1-chloro-3-pentanone, 32830-97-0; propionyl chloride 1:1 complex with aluminum chloride, 36379-65-4; neohexyllithium, 6909-52-0; *tert*-butyllithium, 594-19-4.

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Basicity of the Carbonyl Group. V. Applicability of the Taft–Pavelich Equation to Cyclic Systems with Reference to the Complexation Enthalpy of Cyclic Ketones Using Boron Trifluoride

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Experimental calorimetric data verify the Taft–Pavelich equation for inductive and steric effects in substituted five- and six-membered rings.

The use of linear free energy relationships of the form $\log k/k_0 = \rho^*\sigma^* + \delta E_s$ (I) (the Taft–Pavelich equation) has spread to numerous fields of experimental science[1] since the initial work of Taft[2] on the separation of the polar and steric effects of substituents.

We have recently shown[3] that eq II

$$\Delta H^0_R = (3.74 \pm 0.22)\,\sigma^* - (0.77 \pm 0.17)E_s - 18.21 \text{ kcal mol}^{-1} \quad \text{(II)}$$

can be applied in a satisfactory manner to the reaction enthalpy of CH_3COR ketones with boron trifluoride over a

Table I
Complexation Enthalpies (kcal mol^{-1}) of Saturated Cyclic Ketones

Ketone	$\Sigma\sigma^{*\,a}$	$-\Delta H^0_{\rm calcd}$ ^{b}	$-H^0_{\rm exp}$ ^{c}	$\Delta H^0_{\rm exp} - \Delta H^0_{\rm calcd}$	h^d	δE_s ^{e}	Registry no.
Cyclopentanone	−0.200	19.29	18.94 ± 0.10	0.35	0	0	120-92-3
2-Methyl-	−0.290	19.62	18.83 ± 0.21	0.79	0.44	0.36 ± 0.08	1120-72-5
2,2-Dimethyl-	−0.400	20.04	18.20 ± 0.09	1.84	1.49	1.19 ± 0.26	4541-32-6
2,3-Dimethyl-	−0.310	19.70	18.93 ± 0.27	0.77	0.42	0.36 ± 0.08	14845-37-5
2,4,4-Trimethyl-	−0.315	19.72	18.90 ± 0.07	0.82	0.47	0.36 ± 0.08	4694-12-6
2,2,4-Trimethyl-	−0.415	20.09	18.31 ± 0.24	1.78	1.43	1.19 ± 0.26	28056-54-4
Cyclohexanone	−0.230	19.40	18.62 ± 0.20	0.78	0.07	0	108-94-1
2-Methyl-	−0.325	19.76	18.54 ± 0.19	1.22	0.51	0.36 ± 0.08	583-60-8
3-Methyl-	−0.240	19.44	18.85 ± 0.11	0.59	−0.12	0	591-24-2
4-Methyl-	−0.260	19.51	18.90 ± 0.31	0.61	−0.10	0	589-92-4
2,2-Dimethyl-	−0.425	20.13	18.04 ± 0.18	2.09	1.38	1.19 ± 0.26	1193-47-1
3,3,5-Trimethyl-	−0.290	19.62	18.77 ± 0.09	0.85	−0.14	0	873-94-9

[a] Values taken from ref 1 and 2 or calculated by the method of W. A. Seth Paul and A. Van Duyse, *Spectrochim. Acta, Part A,* 28, 211 (1972). [b] Calculated by means of eq II. [c] Experimental value, and 95% confidence interval (0.5 *M* in CH_2Cl_2). The experimental method has been described: J. F. Gal, L. Elegant, and M. Azzaro, *Bull. Soc. Chim. Fr.,* 1150 (1973); 411 (1974). [d] Difference between the value ($\Delta^{+}H_{i}{}^{0}{}_{\rm exp} - \Delta H^0_{\rm calcd}$ for the α-substituted and the α-unsubstituted ketone (0.35 kcal for the cyclopentanone and mean value of 0.71 kcal for cyclohexanones). [e] Calculated steric effect; see text.

Table II
Complexation Enthalpies (kcal mol^{-1}) of 1-Cyclohexen-2 one

Ketone	$\Sigma\sigma^{*a}$	$-\Delta H^0_{\rm calcd}$ ^{b}	$-\Delta H^0_{\rm exp}$ ^{c}	$\Delta H^0_{\rm exp} - \Delta H^0_{\rm calcd}$	h^d	δE_s ^{e}	Registry no.
1-Cyclohexen-2 one	+0.210	17.75	19.53 ± 0.19	−1.78	+0.11	0	930-68-7
5,5-Dimethyl-	+0.195	17.81	19.60 ± 0.24	−1.79	+0.10	0	4694-17-4
4-Methyl-	+0.185	17.85	19.70 ± 0.09	−1.85	+0.04	0	5515-76-4
4,4-Dimethyl-	+0.150	17.98	20.10 ± 0.26	−2.12	−0.23	0	1073-13-8
4,4,6-Trimethyl-	+0.050	18.39	19.47 ± 0.19	−1.08	+0.81	0.36 ± 0.08	13395-73-8
4,4,6,6-Tetramethyl-	−0.060	18.76	19.37 ± 0.22	−0.61	+1.28	1.19 ± 0.26	32264-57-6
3-Methyl-	−0.115	18.97	21.40 ± 0.04	−2.43	+0.06	0	1193-18-6
3,5-Dimethyl-	−0.125	19.01	21.60 ± 0.22	−2.59	−0.10	0	1123-09-7
3,5,5-Trimethyl-	−0.165	19.16	21.60 ± 0.16	−2.44	+0.05	0	78-59-1

[a-e] See Table I.

range of 4.5 kcal (correlation coefficient 0.9833, standard deviation 0.30 kcal, number of data points 14, confidence level ≫99%).

In the present communication, we demonstrate that eq II can be used to analyze the variation in the reaction enthalpies of methylcyclopentanones, -cyclohexanones, and -cyclohexenones[4] with BF_3 by separating the inductive and steric effects of the substituents.

Our analysis of the contribution of the inductive effect of the methylene groups of the ring is based on two hypotheses.

(1) The inductive effect is equal to the effects of two "pseudo-substituents" obtained by dividing the ring with a plane passing through the C–O bond axis and bisecting the carbonyl π bond. If a carbon atom occurs in this plane, it is included in each of the two pseudo-substituents.

(2) The inductive effects of the two pseudo-substituents are additive toward the carbonyl group.

The additivity of the inductive effects is a well-known experimental fact. For example, the ionization potential of R_1COR_2 ketones is linearly related to ($\sigma^*_{R_1} + \sigma^*_{R_2}$).[5]

Moreover, the ionization potentials of 3-pentanone and of cyclopentanone as well as those of 4-heptanone and of cyclohexanone are practically identical. This justifies the mode of separation adopted.

The σ^* parameters for the five- and six-membered rings have been evaluated elsewhere;[6] they are only slightly different from the $\Sigma\sigma^*$ (pseudo-substituents).

Using the ρ^* value obtained for aliphatic ketones and the reaction enthalpy of acetone (taken as the reference Lewis base) $\Delta H^0_0 = -18.54$ kcal mol^{-1}, we can calculate a $\Delta H^0_{\rm calcd}$ (Table I) in which the steric effect is identical with that of the reference compound. The difference $\Delta H^0_{\rm exp} - \Delta H^0_{\rm calcd}$ is remarkably constant *for an identical substitution α to the carbonyl group in the same ring.* For cyclopentanone itself, this value is 0.35 kcal and the average for the four cyclohexanones which are not substituted at the α position is 0.71 kcal. The smaller experimental reactivities of the rings compared to the calculated ones may be the result of the approximation of the inductive effect or of a more marked steric effect in the rings relative to acetone. The latter alternative is the most likely: it is known that the steric effect increases in going from an aliphatic system to a cyclic system and then to a bicyclic system.[7]

Qualitatively, a steric effect in the same order can be obtained by examining the values of E_s—E_s(i-Pr) < E_s (cyclopentyl) < E_s (cyclohexyl)[2]—or the values of E_s calulated for the polymethylene cyclic groups.[8]

$$E_s^c\ (CH_2)_4 = -0.04;\ E_s^c(CH_2)_5 = -0.15$$

If this contribution to ΔH^0_R due to cyclization is deduced from the values $\Delta H^0_{\rm exp} - \Delta H^0_{\rm calcd}$ for the α-substituted carbonyl compounds, the steric effect of these substituents can be obtained (Table I, column h). For an α-methyl group, we obtain a contribution of 0.44 ± 0.03 kcal (average for cyclopentanones) and of 0.51 kcal (2-methylcyclohexanone). For *gem*-dimethyl substitution, we obtain 1.46 ± 0.03 kcal (average for 2,2-dimethylcyclopentanones) and 1.38 kcal (2,2-dimethylcyclohexanone). These values are remarkably close for the two types of rings and correspond, moreover, to the product δE_s, taking the δ value of eq II, E_s (α-methyl) = E_s (i-Pr) and E_s (α-dimethyl) = E_s (t-Bu) (Table I, last column).

The equation obtained for aliphatic ketones is therefore applicable to analogous cyclic systems (i.e., substituted on one side of the carbonyl group).

Equation II cannot be applied[3] to ketones bearing substituents situated on both sides of the carbonyl group, because the angle of the $C{=}O \rightarrow B$ bond differs from 180°.[9] The steric effect with regard to BF_3 is therefore not additive and much greater in these systems.

Taking into account the cyclization effect, we obtain

$$\Delta H^0_R = 3.74\ \Sigma\sigma^*\ \text{(pseudo-substituents)} - 0.77E_s + \Delta H^0_0 \qquad \text{(III)}$$

with $\Delta H^0_0 = -18.19$ kcal mol^{-1} for the cyclopentanones and -17.83 kcal mol^{-1} for the cyclohexanones, taking into account the conventions used previously for the values of σ^* and E_s.

Equation III reproduces the values of the ΔH^0_{exp} within the limits of accuracy of eq II.

The same method has been applied to the complexation enthalpies of cyclohexenones (Table II).[10]

In this series, one can equally observe the constancy of the term $\Delta H^0_{exp} - \Delta H^0_{calcd}$ for an identical substitution α to the carbonyl group and to the double bond. The latter assumes a negative value because of the increase in basicity due to conjugation with the carbonyl. This effect is increased by the substitution of the double bond by a methyl group in position 3. The calculated steric effect (Table II, column h) is similar to that obtained with saturated ketones. Equation III can therefore be used with $\Delta H^0_0 = -20.43$ kcal mol^{-1} (-21.03 for a methyl group in position 3).

In conclusion, our method of analysis of inductive and steric effects in these ring systems enables us to calculate the complexation enthalpies of cyclic ketones with BF_3 with a very fair degree of accuracy, comparable to that of experimental values. Recently, others approaches have been proposed for the evaluation of steric or inductive effects in cyclic compounds: computation by molecular mechanics[11] or from experimental data.[12]

We feel that an important result of our work is the demonstration that only "classical" parameters (σ^*, E_s) are necessary to describe the basicity of aliphatic and cyclic ketones, using the same Taft–Pavelich equation. It has also been stated that E_s values will correlate structural or reactivity data provided that the concerned groups are in a structural surrounding which does not induce an important conformational preference of the group.[13] In our case, the cyclization of the alkyl chain reduces the steric effect to that of atoms or groups close to the function, i.e., at the α position of the carbonyl. This effect is thus easily evaluated from an equivalent substituent. Work is in progress on several series of mono- and bicyclic carbonyl compounds containing substituents possessing a wider range of inductive and steric effects. The behavior of more hindered systems such as t-BuCOR ketones is also under investigation.

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