(1967).
(27) Not unexpected since the increase in total strain for one additional trigonal center in a four-membered ring is only about 1 kcal/mol.[28]
(28) K. B. Wiberg and R. A. Fenoglio, *J. Am. Chem. Soc.*, **90**, 3395 (1968).
(29) Most nonhalogenated ketenes are formed from acyl halides by way of acylammonium salt intermediates.[30-32]
(30) H. Adkins and Q. E. Thompson, *J. Am. Chem. Soc.*, **71**, 2242 (1949).
(31) D. Cook, *Can. J. Chem.*, **40**, 2362 (1962).
(32) W. T. Brady and G. A. Scherubel, *J. Am. Chem. Soc.*, **95**, 7447 (1973).
(33) We are grateful to Professor W. T. Brady and Dr. G. A. Scherubel for performing these calculations for us.
(34) We thank Professor Owen Asplund for drawing our attention to this potential.
(35) For a review see P. A. Grieco, *Synthesis*, 67 (1975).
(36) We thank Professor Ulrich Hollstein for making the mass spectral measurements.
(37) H. M. McNair and E. J. Bonelli, "Basic Gas Chromatography", Varian Aerograph, Walnut Creek, Calif., 1968, pp 140–142.
(38) The response factors for compounds **3** and **4** were equal, within our experimental error.
(39) Eu(fod)$_3$ is europium(III) tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione).
(40) The low-wavelength absorption may be analogous to the weak charge transfer band of norbornen-5-one.[41-43]
(41) J. Meinwald, S. L. Emerman, N. C. Yang, and G. Buchi, *J. Am. Chem. Soc.*, **77**, 4401 (1955).
(42) P. D. Bartlett and B. E. Tate, *J. Am. Chem. Soc.*, **78**, 2473 (1956).
(43) C. H. DePuy and P. R. Story, *J. Am. Chem. Soc.*, **82**, 627 (1960).
(44) The ratio of *exo*-**5** to *endo*-**5** observed from hydrogenation of the 60:40 **2**:**4** mixture, together with that measured from hydrogenation of pure **4**, allows the estimation that vinylketene cycloadds to 1,3-cyclopentadiene with better than 99% endo vinyl stereospecificity.

Metalation Reactions. 18. Polymetalation Substituted Acetophenones

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The lithium enolates of methyl-substituted acetophenones are metalated further by butyllithium in the presence of TMEDA to di- and trilithium derivatives. The sequence of preferential proton abstraction is *o*-methyl > *o*-H > *p*-methyl > *m*-methyl. A second proton can also be abstracted from the carbon α to the carbonyl group. The compound dilithiated α to the carbonyl undergoes a lithium oxide elimination to yield an acetylene. Abstraction of two protons from two *o*-methyl groups, or from one *o*- and one *p*-methyl groups, or from one *o*-methyl group and the α-methylene group, was also observed. The directive effects in these metalations are discussed in terms of charge alternation.

A preferential proton abstraction by base in hexamethylphosphoric triamide from the *p*-methyl group in 4-methylacetophenone (I) was reported by Dubois.[1] On the other hand, abstraction of two protons from the methyl α to the carbonyl in 2,4,6-trimethylacetophenone (II) by butyllithium was claimed.[2] This last result was not entirely reliable, since it was proved only by the production of III, which contained two deuterium atoms in the acetyl group, as confirmed by the NMR spectrum. However, the second proton could have been exchanged during the deuteration.

Our interest in polymetalation[3] has prompted us to investigate the possibility of polymetalation of the substituted acetophenones. Several other ketones such as acetophenone (IV), 2- (V) and 3-methylacetophenone (VI) were studied in addition to I and II.

In order to avoid the attack of butyllithium on the carbonyl group, it was necessary (except in the case of 2,4,6-trimethylacetophenone, that was hindered enough to avoid addition of butyllithium to the carbonyl group) to carry out the abstraction of the first proton with a different base to form the enolate. The following procedure was adopted. The enolates, obtained by the action of sodium hydride or lithium diisopropylamide on the ketones, were converted into trimethylsilyl enol ethers. Addition of 1 equiv of butyllithium to a solution of these o ethers transformed them into lithium enolates.[4] Further metalation of these enolates was performed by an excess of butyllithium in the presence of TMEDA.

Results

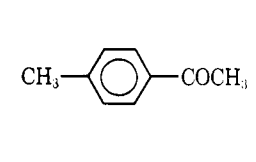
Metalation of II with butyllithium in hexane–TMEDA and subsequent treatment with trimethylchlorosilane yielded the disilyl (VIIb) and two trisilyl (VIIIb and IXb) derivatives, that are the products of the reaction of the dilithium (VIIa) and the trilithium (VIIIa and IXa) intermediates. Hydrolysis of these derivatives gave the corresponding ketones Xb, XIb, and XIIb.

The metalation of II in ether made it possible to follow by NMR the transformation of II into XIIIa and, after the addition of TMEDA, the further lithiation to VIIa. In the first stage the signals of XIIIa appeared: aromatic at 6.63 (s), $=CH_2$ at 3.9 (s, 1 H) (the second vinylic proton was hidden by ether), the *o*-methyls at 2.24 (s), and the *p*-methyl at 2.07 ppm (s). These signals disappeared on further metalation, giveing place to two aromatic signals at 5.37 (s) for the proton para and at 59.97 ppm ortho to the CH_2Li. Meta coupling was observed by broadening of the singlets. The intensity of the *o*-methyls singlet was reduced and a new singlet for the CH_2Li appeared at 1.84 ppm. (s). Silylation of the ether solution led to VIIb. Similar results were obtained in THF (without TMEDA), but with an additional minor product XIVb formed by metalation of the *p*-methyl and subsequent silylation and hydrolysis of the enol ether.

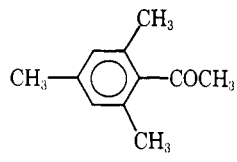
The appearance of two aromatic signals in the product of dimetalation proved its structure VIIa, since ring metalation or at the *p*-methyl would have led to a product showing one aromatic signal only. Quenching of the enolate XIIIa with D_2O in our hands led to a mixture of mono-, di-, tri-, and undeuterated products in the α-methyl group as shown by he M^+ peaks obtained in the mass spectrum. In our conditions, the reported[2] dideuterated II was not the product of dimetalation, but an artifact of exchange.

Preferential ring metalation at the position ortho to the enolate group was obtained on metalation of XVb in hexane–TMEDA. Treatment of the product of metalation with trimethylchlorosilane yielded preponderantly XVIb and two products of dimetalation, XVIIb (9%) and XVIIIb (10%). A small amount of an unidentified product was also formed.

The metalation at the ortho position was proved by the NMR of the ketone, product of deuterolysis of the metalated mixture. Instead of the A_2B_2 pattern of the aromatic protons in I, there appeared one proton only at the ortho position in this product. Metalation of XVb with butyllithium in THF

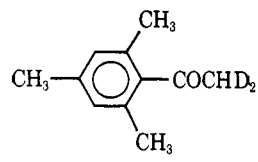


I



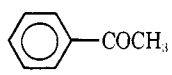
II

a, R = Li
b, R = $Si(CH_3)_3$



III

c, R = K
d, R = $OCOCH_3$



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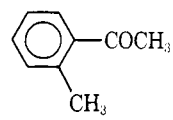
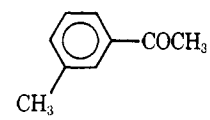


V



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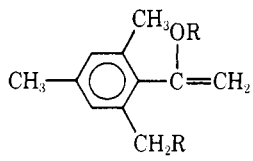

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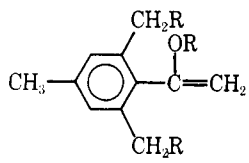

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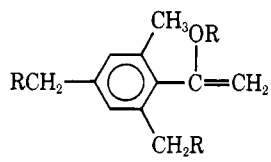

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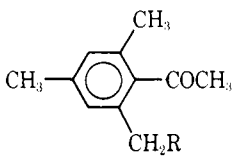
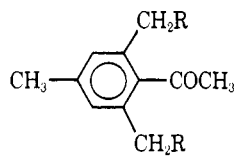


X



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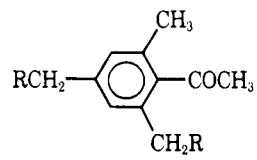

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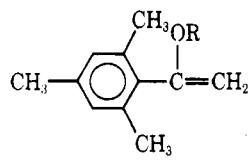

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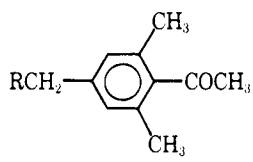

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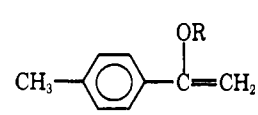

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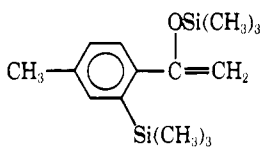

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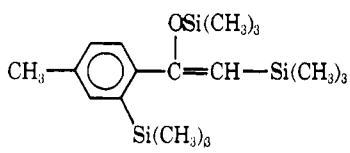

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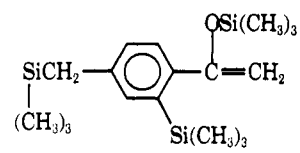


XVIII

and subsequent treatment with trimethylchlorosilane and hydrolysis yielded XIXb as the major product derived from the product of metalation at the *p*-methyl XIXa.

Metalation of the trimethylsilyl ether XXb derived from IV gave one product only, XXIa, metalated at the ortho position. Silylation of the product of metalation yielded XXIb. Alkylation of XXIa with methyl bromide gave a mixture of 2-methylacetophenone (V), 2-methylpropiophenone (XXII), and 2-methylisobutyrophenone (XXIII). The two ketones V and XXIII were products of transmetalation during the alkylation. The occurrence of transmetalation was proved by treatment of the enolate of 2-methylacetophenone with methyl bromide, that yielded the starting material, XXII, and XXIII.

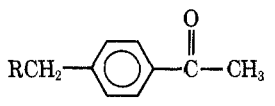
A mixture of products was obtained on metalation of the silyl ether XXIVb of V and subsequent treatment with trimethylchlorosilane, the most abundant being XXVb. In addition, there was obtained XXVIb, formed from the product of dimetalation XXVIa at the *o*-methyl, XXVIIb from the product of dimetalation XXVIIa at the methyl α to the carbonyl, and an acetylenic derivative XXVIIIb devoid of oxygen. XXIX was clearly formed by elimination of lithium oxide from the intermediate XXVIIa yielding then XXVIIIa with butyllithium and subsequently XXVIIIb with trimethylchlorosilane. An intermediate formed by abstraction of the lost proton from the carbon α to the carbonyl in XXVIIa is less probable.

No attack on the methyl was observed in the reaction of the enolate of VI, that yielded a product XXXIa of metalation at the ortho position exclusively and XXIb on subsequent treatment with trimethylchlorosilane. The NMR spectrum of this compound in the aromatic range consisted of a doublet, part of an AB signal at 7.35, and a not well-separated doublet at ~7 ppm, as well as a singlet at ~7.05. Hydrolysis of the enol silyl group of XXXIb to the ketone XXXII confirmed the structure assigned. The NMR spectrum of XXXII showed a doublet at 7.22 (1 H, J = 8 Hz), showing additional splitting of 2 Hz by a meta proton, a doublet at 7.52 (1 H, J = 8 Hz), and a singlet at 7.58 ppm (1 H, br s). Addition of $Eu(fod)_3$ produced a better resolved spectrum. The low-field singlet of the proton ortho to the carbonyl was shifted to lowerfield and the aromatic pattern showed in addition to it two doublets of the AB system. Deuterolysis of XXXIa introduced deuterium also at the ortho position. Alkylation with methyl bromide yielded a mixture of XXXIII, XXXIV, and XXV, which were separated and their structure determined by NMR. The aromatic pattern in the NMR spectra of these ketones showed a singlet (1 H) at lower yield, and a higher field singlet (2 H) in agreement with the NMR spectra of a series of similar compounds[3,5] with a 1,2,4-trisubstituted benzene ring. The NMR spectra

Table I. Products of Metalation–Silylation of Acetophenones

Substrate	Solvent	Catalyst: Ratio 1; ratio 2[a]	Duration of metalation, h	Products
II	Hexane	TMEDA: 4; 4	24	VII (56%); VIII (22%); IX (11%); 11% not identified.
II	Hexane	TMEDA: 2; 2	24	XIII (23%); VII (77%)
II	Hexane	TMEDA: 4; 1	48	VII (45.5%); VIII (34.5%); IX (17%)
II	THF	–: 4; –	24	II (28%); X (62.5%); XIV (9%)
II	THF	*i*-Pr_2NLi: 4; –	24	XIII (90%)
XV	Hexane	TMEDA: 4; 2	24	XVI (71%); XVII (10%); XVIII (10%)
XV	THF	–: 4; –	24	I (50%); XIX (50%)
XX	Hexane	TMEDA: 4; 2	24	XXI (90%)
XX[b]	Hexane	TMEDA: 4; 2	24	IV (8%); V (34%); XXII (26%); XXIII (26%)
XXIV	Hexane	TMEDA: 4; 2	24	XXV (55%); XXVIII (20%); XXVI (13%); XXVII (6.5%)
XXIV	Hexane	TMEDA: 4; 1	24	XXV (85%)
V[b]	THF	*i*-Pr_2NLi: 1; –	1	V (25%); XXII (50%); XXIII (25%)
XXX	Hexane	TMEDA: 4; 2	24	XXXI (90%)
XXX	Hexane	TMEDA: 4; 1	24	XXXI (90%)
XXX[b]	Hexane	TMEDA: 4; 1	24	VI (7.5%); XXXIII (24.5%); XXXIV (18%); XXXV (38%)

[a] Ratio 1, between BuLi considered as a monomer, and the substrate; ratio 2, between BuLi and TMEDA. [b] Alkylation with methyl bromide was performed instead of silylation.



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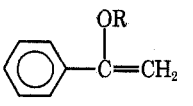

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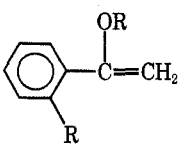
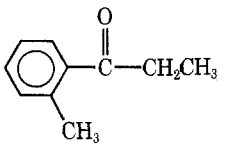


XXI



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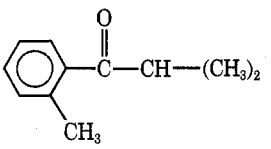
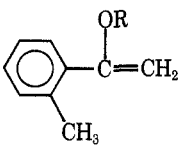


XXIII



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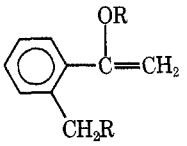

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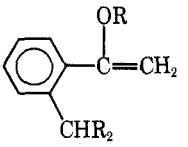

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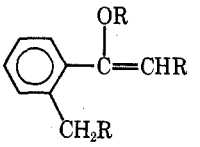

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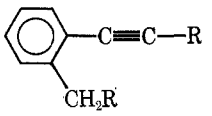

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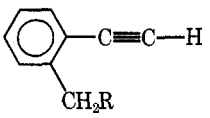

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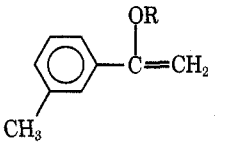

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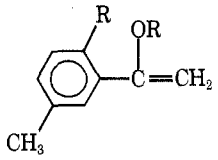

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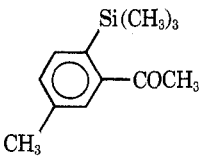

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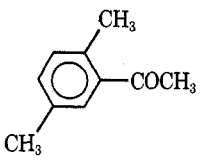
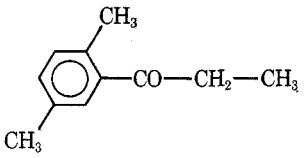
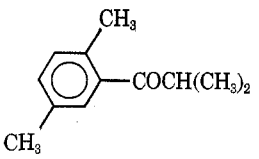


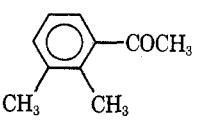
XXXIII



XXXIV



XXXV



XXXVI

of these ketones were resolved in the presence of $Eu(fod)_3$, and in all of them the signals of the aromatic protons consisted of a singlet shifted to low field (1 H) and an AB quartet (2 H) in the usual aromatic range. The other possible isomeric products, e.g., 2,3-dimethylacetophenone (XXXVI), would have shown an entirely different pattern in the NMR spectrum.

Metalation of XXXb in ether made it possible to follow its transformation into the enolate XXXa, and, after the addition of TMEDA, the further lithiation to XXXIa. In the first stage, the signals of the enolate appeared: aromatic at 6.78–7.24 (m), $=CH_2$ at 3.91 (s) and 3.62 (s), and the methyl at 2.11 ppm (s). These signals disappeared on further metalation, giving place

to an interesting pattern in the aromatic range: two doublets each of 1 H at 7.70 and at 6.66 ppm (J = 6 Hz), and a singlet (1 H) at 7.14 ppm. This spectrum confirmed the structure XXXIa, in which one proton ortho to the lithium is shifted to lower field[6] 7.70, and coupled with its neighbouring proton at 6.66 ppm. The proton between the enolate and the methyl appears as a singlet. Meta coupling was observed by broadening of the singlet and the higher field doublet.

Metalation with lithium diisopropylamide of an o-methyl in benzamides was reported.[7] However, no such metalation could be performed by us in the case of the enolates studied here.

Discussion

The lithium enolates of aryl methyl ketones undergo further metalation in ether–TMEDA, despite the negative charge of the side chain, which is also partially delocalized into the aromatic ring. Abstraction of two additional protons with organolithium compounds is observed in hexane–TMEDA. These metalations are strongly directed to the position ortho to the enolate, with a methyl at this position being metalated preferentially to the carbon ortho in the ring. These enolates therefore enter the class of directing groups in the metalation like amides[7-10] or benzylamines.[11-14] Chelation is probably the driving force for ortho metalation. The observation that abstraction of an additional proton occurs at the carbon of the side chain α to the carbonyl is of great interest. This is the first case observed for dimetalation of a methyl α to the carbonyl. Metalation is also observed in the p-, but not at the m-methyl.

We have therefore an additional directing effect to that for metalationat the ortho position. This effect discriminates between the m- and p-methyls, and we ascribe it to the preference shown by conjugated systems to introduce additional charges on the same set of starred carbons, conserving in that manner the charge alternation that was present in the initial odd alternating ion. This can occur when a proton is abstracted from a p- but not a m-methyl. The same charge alternation is maintained after an additional abstraction of a proton from the carbon α to the carbonyl, or from the o-methyl in preference to that from the ortho carbon. The preference for creating polyanions by proton abstraction in such a manner as to create conjugated systems with charge alternation was observed previously in olefins leading to trimethylenemethane dianions,[15] to allyl dianion,[16] add to propargylic di-[17] and trianions.[18] In the last case, proton abstraction was shown to occur three times consecutively from the same carbon rather than from the other propargylic position that would have led to a more even charge distribution.

The influence of chelation and its dependence on the solvent is illustrated by the preferential metalation of the enolate of 4-methylacetophenone at the ortho position in hexane–TMEDA and at the p-methyl in THF. It was observed before[19] that TMEDA solvates lithium salts of delocalized carbanions very strongly externally to a solvated tight ion pair, but THF can produce solvent separated ion pairs. The cation in the solvent separated ion pair is obviously less effective in chelation, and the electronic effects, that prefer charge alternation, are therefore determining in THF the position of proton abstraction. The coordination of the cation in the tight ion pair with one molecule of TMEDA only, thus leaving a site on the lithium free for chelation, may be an additional reason for the difference between the chelating efficiency of lithium in the presence of TMEDA and THF. In THF solution all the available sites on the lithium cation of an ion pair are probably coordinated with this ligand. The chelation through a separated ion pair in THF is sufficient to prefer metalation at the o- to that at the p-methyl, since in both reactions an ion with charge alternation is formed. However, the metalation rate at the p- relative to the o-methyl is larger in THF that in hexane–TMEDA, where tight ion pairs are present.

Steric effects intervene also in the metalation promoted by chelation. The attack on the enolate of 3-methylacetophenone by butyllithium takes place exclusively at the ortho position away from the ring methyl.

A charge in a π-conjugated system not only does not prevent the addition of further charges to this system, if the charge is introduced on the same set of starred atoms,[3,17,18,20] but makes it sometimes easier than the introduction of the first charge. Abstraction of a proton to create a carbon–metal σ bond that is perpendicular to the π system containing a charge is not prevented. It is of interest hat the presence of such a carbon–metal bond in aryllithium compounds interferes not only with further metalation by abstraction of protons of the ring and the formation of additional σ carbon–lithium bonds in the same plane as the first one, but also with the introduction of charges into the perpendicular π system,[21] if the C–Li bond is on a carbon belonging to the unstarred set.

The conjugation between the enolate group and the ortho or para benzylic methylenes in the polyanions is of the crossed-conjugation type. This kind of conjugation was found to be more stable than the linear one in the polyanions, e.g., trimethylenemethane dianion[15,20] relative to butadiene dianion or m-xylylene dianion relative to its para isomer.[3,5]

Experimental Section

NMR spectra of all compounds except the lithium derivatives were recorded in CCl_4 on a Varian T60 apparatus using Me_4Si as an internal standard. Gas chromatographic separations were performed on a Varian Aerograph A-90-P-3. Ir spectra were recorded on a Perkin-Elmer 337, and uv spectra on Unicam SP 800A spectrophotometers. Analyses were performed by Mrs. M. Goldstein of the Microanalytical Laboratory of the Hebrew University.

2,4,6-Trimethylacetophenone, 4-methylacetophenone, 3-methylacetophenone, 2-methylacetophenone, and acetophenone were commercial samples (Aldrich) that were tested by us by GLC.

The enol silyl ethers were prepared by the procedure recommended by Stork[4] using sodium hydride, but better yields were obtained when lithium diisopropylamide[22] was used as the base for proton abstraction. The first but not the second procedure failed with m-methylacetophenone.

An example for the general procedure for preparation of the enol silyl ethers is given for m-methylacetophenone.

Butyllithium (35 ml, 1.5 M) was added dropwise to 6.5 ml of diisopropylamine in 20 ml of dry THF under an inert atmosphere and cooled to 0 °C in an ice bath; then 5 g of VI was added. After the addition was complete, the mixture was left for 30–60 min at 0 °C; then 5.5 g of trimethylchlorosilane was added. After 30 min the reaction mixture was filtered. The organic phase was washed rapidly with water and an aqueous solution of sodium bicarbonate. After evaporation of the solvent, the residue was distilled at 110–120 °C (25 mm), yield 6.5 g (84%) of [1-(m-methylstyryl)oxy]trimethylsilane (XXX): NMR δ 7.08–7.05 (m, 4 H, ArH), 4.85 (s, 1 H, =CH), 4.38 (s, 1 H, =CH), 2.40 (s, 3 H, $ArCH_3$), 0.28 [s, 9 H, $OSi(CH_3)_3$]. Anal. Calcd for $C_{12}H_{18}SiO$: C, 69.9; H, 8.7. Found: C, 69.61; H, 8.68. Ir 850, 1020, 1250, 1310, 1490, 1590, 1600, 1620 cm^{-1}. The other enol silyl ether derivatives were obtained by this procedure.

[1′-(2,4,6-Trimethylstyryl)oxy]trimethylsilane (XIII): NMR δ 6.68 (s, 2 H, ArH), 4.54 (s, 1 H, =CH), 4.11 (s, 1 H, =CH), 2.34 (s, 3 H, $ArCH_3$), 0.28 [s, 9 H, $OSi(CH_3)_3$]; m/e 162 [$M^+ - Si(CH_3)_3$].

[1-(p-Methylstyryl)oxy]trimethylsilane (XV): NMR δ 7.01 (d, J = 8 Hz, 2 H, ArH), 7.38 (d, J = 8 Hz, 2 H, ArH), 4.75 (d, J = 2 Hz, 1 H, =CH), 4.35 (d, J = 2 Hz, 1 H, =CH), 2.35 (s, 3 H, $ArCH_3$), 0.21 [s, 9 H, $OSi(CH_3)_3$]. Anal. Calcd for $C_{12}H_{18}SiO$: C, 69.9; H, 8.7. Found: 69.7, H, 8.9. Ir 850, 1020, 1250, 1620 cm^{-1}.

[1-(Phenylvinyl)oxy]trimethylsilane (XX): NMR δ 7.61–7.15 (m, 5 H, ArH), 4.83 (d, J = 2 Hz, 1 H, =CH), 4.36 (d, J = 2 Hz, 1 H, =CH), 0.25 [s, 9 H, $OSi(CH_3)_3$]. Anal. Calcd for $C_{11}H_{16}OSi$: C, 68.7; H, 8.3. Found: C, 68.90; H, 8.64, Ir 850, 1010, 1120, 1250, 1320, 1620 cm^{-1}.

[1′-(2-Methylstyryl)oxy]trimethylsilane (XXIV): NMR δ 7.08–7.05 (m, 4 H, ArH), 4.85 (d, J = 2 Hz, 1 H, =CH), 4.38 (d, J = 2 Hz, 1 H, =CH), 2.40 (s, 3 H, $ArCH_3$), 0.28 [s, 9 H, $OSi(CH_3)_3$]. Anal. Calcd for

$C_{12}H_{18}SiO$: C, 69.9; H, 8.7. Found: C, 69.80; H, 8.86. Ir 850, 1020, 1090, 1140, 1250, 1270, 1310, 1620 cm^{-1}.

Metalation. All metalations were carried out by a standard procedure. An example for XXX is given. To 13 ml of 1.5 M butyllithium in hexane under an inert atmosphere and cooled to −20 to −30 °C, 2.6 ml of TMEDA was added, and then 1 g of XXX. The reaction mixture was left at room temperature for 24 h, then cooled to 0 °C in an ice bath and 5 g of trimethylchlorosilane was added. The reaction mixture was left at room temperature for several hours, then filtered and the organic solution washed rapidly with water. The solvent was evaporated and the product in the residue (1.4 g) separated by preparative GLC at 180 °C on a 2 m × 0.25 in. column of 15% SE-30 on Chromosorb W, mesh size 60/80. The following products of metalation and subsequent silylatiion were obtained in this manner.

[1-(2′-Trimethylsilylmethylene-4′,6′-dimethylsytryl)oxy]trimethylsilane (VII): NMR δ 6.64 (brs, 2 H, ArH), 4.54 (s, 1 H, =CH), 4.11 (s, 1 H, =CH), 2.28 (s, 6 H, $ArCH_3$), 2.21 (s, 2 H, $ArCH_2Si$), 0.18 [s, 9 H, $OSi(CH_3)_3$], −0.03 [s, 9 H, $CH_2Si(CH_3)_3$]; *m/e* 234 [M^+ − $Si(CH_3)_3$]; ir 850, 1050, 1080, 1170, 1250, 1300, 1600, 1620 cm^{-1}. Anal. Calcd for $C_{17}H_{30}OSi_2$: C, 66.3; H, 9.8. Found: C, 66.38; H, 9.96.

[1-Bis(2′,6′-trimethylsilylmethylene)-4-methylstyryl)oxy]trimethylsilane (VIII): NMR δ 6.51 (s, 2 H, ArH), 4.47 (s, 1 H, =CH), 4.07 (s, 1 H, =CH), 2.21 (s, 3 H, $ArCH_3$), 2.14 (s, 2 H, $ArCH_2Si$), 0.21 [s, 9 H, $OSi(CH_3)_3$], −0.06 [s, 9 H, $CH_2Si(CH_3)_3$]; *m/e* 306 [M^+ − $Si(CH_3)_3$]; ir 850, 1050, 1075, 1160, 1250, 1300, 1620 cm^{-1}. Anal. Calcd for $C_{20}H_{38}OSi_3$: C, 63.4; H, 10. Found: C, 63.42; H, 10.33.

[1-(2′-Trimethylsilyl-4′-methylstyryl)oxy]trimethylsilane (XVI): NMR δ 7.14 (s, 1 H, ArH), 4.32 (brs, 2 H $=CH_2$), 2.34 (s, 3 H, $ArCH_3$), 0.31 [s, 1 H, $ArSi(CH_3)_3$], 0.21 [s, 9 H, $OSi(CH_3)_3$]; ir 845, 1255, 1260, 1260 cm^{-1}. Anal. Calcd for $C_{15}H_{26}OSi_2$: C, 64.7; H, 9.36. Found: C, 64.65; H, 9.27.

1-(Trimethylsiloxy)-2-(trimethylsilyl)-1-(2′-trimethylsilyl-4′-methylphenyl)ethylene (XVII): NMR δ 7.09 (s, 1 H, ArH), 6.93 (s, 2 H, ArH), 4.41 (s, 1 H, =CH), 2.37 (s, 3 H, $ArCH_3$), 0.30 [s, 9 H, $ArSi(CH_3)_3$], 0.14 [s, 9 H, $OSi(CH_3)_3$], −0.06 [s, 9 H, $=CSi(CH_3)_3$].

[1-(2′-Trimethylsilyl-4′-trimethylsilylmethylenestyryl)oxy]trimethylsilane (XVIII): NMR δ 6.7–6.9 (m, 3 H, ArH), 4.26 (s, 2 H, $=CH_2$), 2.0 [s, 2 H, $CH_2Si(CH_3)_3$], 0.30 [s, 9 H, $ArSi(CH_3)_3$], 0.22 [s, 9 H, $OSi(CH_3)_3$], 0.04 [s, 9 H, $ArCH_2Si(CH_3)_3$].

[1-(2′-Trimethylsilylstyryl)oxy]trimethylsilane (XXI): NMR δ 7.44–7.24 (m, 1 H, ArH), 7.03–7.08 (m, 3 H, ArH), 4.38 (brs, 2 H, $=CH_2$), 0.31 [s, 9 H, $ArSi(CH_3)_3$], 0.21 [s, 9 H, $OSi(CH_3)_3$]; ir 840, 1130, 1260, 1620 cm^{-1}. Anal. Calcd for $C_{14}H_{24}OSi_2$: C, 63.6; H, 9.09. Found: C, 64.31; H, 9.64.

[1-(2′-Trimethylsilylmethylenestyryl)oxy]trimethylsilane (XXV): NMR δ 6.98 (m, 4 H, ArH), 4.41 (s, 1 H, =CH), 4.28 (s, 1 H, =CH), 2.25 (s, 2 H, $ArCH_2Si$), 0.11 [s, 9 H, $OSi(CH_3)_3$], −0.05 [s, 9 H, $ArCHSi(CH_3)_3$]; ir 850, 1015, 1110, 1250, 1310, 1620 cm^{-1}. Anal. Calcd for $C_{15}H_{26}OSi_2$: C, 64.7; H, 9.36. Found: C, 65.1; H, 9.4.

[1-(2′,2′-Bis(trimethylsilylmethylenestyryl)oxy]trimethylsilane (XXVI): NMR δ 6.71–6.81 (m, 4 H, ArH), 4.25 (s, 1 H, =CH), 4.08 (s, 1 H, =CH), 1.98 [s, 1 H, $ArCH(Si)_2$], 0.15 [s, 9 H, $OSi(CH_3)_3$], −0.01 [s, 18 H, $ArCH(Si(CH_3)_3)_2$].

1-(Trimethylsiloxy)-2-(trimethylsilyl)-1-(2′-trimethylsilylmethylene)styrene (XXVII): NMR δ 6.85–6.98 (m, 4 H, ArH), 4.45 (s, 1 H, =CH), 2.21 (s, 2 H, $ArCH_2Si$), 0.15 [s, 9 H, $OSi(CH_3)_3$], −0.01 [s, 9 H, $ArCH_2Si(CH_3)_3$], −0.05 [s, 9 H, $=CSi(CH_3)_3$].

1-(2′-Trimethylsilymethylenephenyl)-2-(trimethylsilyl)acetylene (XXVIII): NMR δ 6.98–7.2 (m, 4 H, ArH), 2.26 (s, 2 H, $ArCH_2Si$), 0.2 [s, 9 H, $\equiv CSi(CH_3)_3$], 0.0 [s, 9 H, $ArCH_2Si(CH_3)_3$]; ir C≡C 2160 cm^{-1}.

[1-(2′-Trimethylsilyl-5′-methylstyryl)oxy]trimethylsilane (XXXI): NMR δ 7.35 (d, J = 6 Hz, 1 H, ArH), 6.96 (d, 1 H, ArH), 7.05 (s, 1 H, ArH), 4.38 (brs, 2 H, $=CH_2$), 2.34 (s, 3 H, $ArCH_3$), 0.21 [s, 9 H, $OSi(CH_3)_3$], 0.24 [s, 9 H, $ArSi(CH_3)_3$]; ir 860, 1020, 1265, 1320 cm^{-1}. Anal. Calcd for $C_{15}H_{26}OSi_2$: C, 64.7; H, 9.3. Found: C, 64.81; H, 9.33.

The hydrolysis of the enol silyl ethers to the corresponding ketones was carried out with *p*-toluenesulfonic acid in an aqueou methanolic solution.[4]

2-Trimethylsilylmethylene-4,6-dimethylacetophenone (X): NMR δ 6.63 (m, 2 H, ArH), 2.31 (s, 3 H, $COCH_3$), 2.23 (s, 3 H, $ArCH_3$), 2.15 (s, 3 H, $ArCH_3$), 1.88 (s, 2 H, $ArCH_2Si$), −0.03 [s, 9 H, $ArCH_2Si(CH_3)_3$]; *m/e* 234 (M^+); ir 850, 1250, 1350, 1700 cm^{-1}. Anal. Calcd for $C_{14}H_{22}OSi$: C, 71.8; H, 9.4. Found: C, 71.99; H, 9.38.

2,6-Bis(trimethylsilylmethylene)-4-methylacetophenone (XI): NMR δ 6.51 (s, 2 H, ArH), 2.35 (s, 3 H, $COCH_3$), 2.27 (s, 3 H, $ArCH_3$), 1.88 (s, 4 H, $ArCH_2Si$), −0.03 [s, 18 H, $Ar[CH_2Si(CH_3)]_2$]; *m/e* 306 (M^+); ir 850, 1150, 1250, 1350, 1420, 1695 cm^{-1}.

2,4-Bis(trimethylsilylmethylene)-6-methylacetophenone (XII): NMR δ 6.51 (m, 2 H, ArH), 2.38 (s, 3 H, $COCH_3$), 2.21 (s, 3 H, $ArCH_3$), 1.98 (s, 2 H, $ArCH_2Si$), 1.91 (s, 2 H, $ArCH_2Si$), 0.02 [s, 9 H, $Si(CH_3)_3$], 0.0 [s, 9 H, $Si(CH_3)_3$]; ir 850, 1160, 1250 1350, 1420, 1690 cm^{-1}; *m/e* 306 (M^+).

Reaction with Methyl Bromide. The metalation mixture was cooled in an acetone–dry ice bath and gaseous methyl bromide was bubbled through the solution for 10 min. The reaction mixture was brought to room temperature and left for several hours. Water was then added, and the organic layer was separated and washed with aqueous 5% hydrochloric acid and with aqueous sodium bicarbonate. The solvent was evaporated and the products in the residue (1.1 g) separated by GLC at 145 ° C on a 2 m × 0.25 in. column of 15% SE-30 on Chromosorb W. The products of metalation and subsequent alkylation of acetophenone were separated preparatively at 155 °C on a 5 m × 0.25 in. column of 20% Carbowax 20m on Chromosorb W, total yield 75%.

2,5-Dimethylacetophenone (XXXIII): NMR δ 7.41 (s, 1 H, ArH), 7.08 (s, 2 H, ArH), 2.3 (s, 3 H, $ArCH_3$), 2.45 (s, 3 H, $ArCH_3$), 2.48 (s, 3 H, $COCH_3$).

2,5-Dimethylpropiophenone (XXXIV): NMR δ 7.38 (s, 1 H, ArH), 7.06 (s, 2 H, ArH), 2.31 (s, 3 H, $ArCH_3$), 2.38 (s, 3 H, $ArCH_3$), 2.8 (q, 2 H, $COCH_2$), 1.15 (t, 3 H, CH_2CH_3).

2,5-Dimethylisobutyrophenone (XXXV): NMR δ 7.28 (s, 1 H, ArH), 7.11 (s, 2 H, ArH), 2.38 (s, 6 H, $ArCH_3$), 3.31 [quintet, 1 H, $CH(CH_3)_2$], 1.13 [d, 6 H, $(CH_3)_3CH$].

2-Methylacetophenone (V): NMR data were compared with a commercial sample (Aldrich).

2-Methylpropiophenone (XXII): NMR δ 7.41–7.61 (m, 1 H, ArH), 7.21 (m, 3 H, ArH), 2.45 (s, 3 H, $ArCH_3$), 2.8 (q, J = 6 Hz, 2 H, CH_2CO), 1.19 (t, 3 H, CH_3CH_2).

2-Methylisobutyrophenone (XXIII): NMR δ 7.41–7.61 (m, 1 H, ArH), 7.21 (m, 3 H, ArH), 2.4 (s, 3 H, $ArCH_3$), 3.3 [quintet, 1 H, $CH(CH_3)_2$], 1.16 [d, J = 6 Hz, 6 H, $(CH_3)_2CH$].

Metalation with Butyllithium in THF. Hexane was evaporated in vacuo from 16.5 ml (24.7 mmol) of a 1.5 M solution of butyllithium in hexane. The residue was cooled in an acetone–dry ice bath and15 ml of dry THF was added. The temperature was brought to 0 °C by changing the dry ice–acetone bath to an ice bath and 1 g of II was added. (The same procedure was used for XV.) Subsequent silylation and isolation of products was performed by the same procedure as described before, but only ketones were isolated from THF.

2,6-Dimethyl-4-(trimethylsilylmethylene) acetophenone (XIVb); NMR δ 6.4 (s, 2 H, ArH), 2.3 (s, 3 H, $COCH_3$), 2.13 (s, 6 H, $ArCH_3$), 1.93 (s, 2 H, $ArCH_2Si$), 0.0 [s, 9 H, $CH_2Si(CH_3)_3$].

4-(Trimethylsilylmethylene)acetophenone (XIXb): NMR δ 7.86 (d, J = 8 Hz, 2 H, ArH), 7.06 (d, J = 8 Hz, 2 H, ArH), 2.53 (s, 3 H, $COCH_3$), 2.2 (s, 2 H, $ArCH_2Si$), 0.0 [s, 9 H, $ArCH_2Si(CH_3)_3$]; *m/e* 206 (M^+); ir 1680 cm^{-1} (C=O).

The NMR spectra of XIIIa, VIIa, XXXa, and XXXIa were recorded by carrying out the metalation of II and XXXb, respectively, in NMR tubes. The metalation was also performed with BuLi in ether in the presence of TMEDA. Under this procedure it was possible to use catalytic amounts of TMEDA and to overcome the difficulties caused by precipitates formed when catalytic amounts of TMEDA in hexane were used. Chemical shifts have been determined relative to added Me_4Si.

The shift reagent used was $Eu(fod)_3$, i.e., tris(6,6,7,7,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium. Small portions of this shift reagent were added to CCl_4 solutions of the samples in NMR tubes until well-resolved spectra were obtained, and addition of further catalytic amounts had no significant influence on the spectra. (Excess must be avoided so as not to cause considerable line broadening.)

Registry No.—II, 1667-01-2; V, 577-16-2; VI, 585-74-0; VIIb, 59796-73-5; VIIIb, 59790-43-1; Xb, 59790-44-2; XIb, 59790-45-3; XIIb, 59790-46-4; XIIIb, 59790-47-5; XIVb, 59790-48-6; XVb, 54731-27-0; XVI, 59790-49-7; XVII, 59790-50-0; XVIII, 59790-51-1; XIXb, 1833-48-3; XXb, 13735-81-4; XXIb, 59790-52-2; XXII, 2040-14-4; XXIII, 2040-21-3; XXIVb, 59790-53-3; XXVb, 59790-54-4; XXVIb, 59790-55-5; XXVIIb, 59790-56-6; XXVIIIb, 59790-57-7; XXXb, 59790-58-8; XXXIb, 59790-59-9; XXXIII, 2142-73-6; XXXIV, 35031-52-8; XXXV, 5445-46-5; trimethylchlorosilane, 75-77-4.

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Solvent and Substituent Effects upon the n → π* Transition of Aliphatic Carboxylic Acids and Esters

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The near-ultraviolet spectra of 13 aliphatic carboxylic acids, 13 ethyl esters, and 16 alkyl acetates were determined for solutions in *n*-hexane, acetonitrile, and water. The carbonyl n → π* transition for these compounds was found in the vicinity of 206 nm under hydrogen-bonding conditions, and around 212 nm in the absence of hydrogen bonding. The spectra of the carboxylic acids in acetonitrile solution showed that the carboxyl group is not involved in hydrogen bonding in this solvent. The absorption band of alkyl acetates was red shifted by increasing bulkiness of the *O*-alkyl group. The values of ϵ_{max} ranged from 40 to 100 and were determined principally by the electron-donating abilities of the *C*-alkyl groups, for both acids and esters. The spectra of these compounds as neat liquids showed a very weak transition ($\epsilon_{max} \simeq 10^{-2}$) in the vicinity of 275 nm.

The electronic absorption spectra of saturated aliphatic carboxylic acids and their alkyl esters display three absorption bands. The best known of these bands is the transition observed between 200 and 220 nm, with a molar absorptivity of 50–60.[1] A variety of arguments have been used to assign this band to the carbonyl n → π* transition of both the acids[2,3] and the esters.[4] In agreement with this assignment, this band in the spectra of esters is blue shifted with increasing solvent polarity.[5] Variation of either the *C*-alkyl or the *O*-alkyl group in the ester structure produces variations in the transition energy which appear to be more closely related to the overall conformation of the molecule than to variation of the electrical effects of these substituents.[5,6]

The n → π* absorption band is superimposed upon the end absorption of a much stronger band with its peak in the vacuum ultraviolet. This absorption band has been studied by Nagakura and his co-workers,[7,8] who found peaks in the range 155–165 nm, with molar absorptivities from 2500 to 4200, in the spectra of the vapors of formic and acetic acids, and of ethyl acetate. Theoretical considerations led these authors to the conclusion that this band is of mixed character, involving intramolecular charge transfer from the singly bonded oxygen to the carbonyl group, combined with a smaller contribution from the π → π* transition of the carbonyl.[8]

In 1931, Hartleb published a study of the absorption spectra of neat liquid carboxylic acids.[9] This study showed the presence of a shoulder on the end absorption, at 270–280 nm. The molar absorptivity at this shoulder was of the order of magnitude of 10^{-2}. The only ester which was examined in the study, tributyrin, failed to show this shoulder, which led Hartleb to the conclusion that the shoulder was due to an absorption band of the carboxylate anion. Since the spectra of salts of carboxylic acids do not show an absorption band in the vicinity of this shoulder, this interpretation is not tenable. No further mention of this shoulder has appeared in the literature.

Although Closson and co-workers[5,6] made an extensive examination of solvent and substituent effects upon the spectra of aliphatic esters, no comparable study of the spectra of the corresponding acids has been described. Since the hydrogen bonding and steric interactions in carboxylic acids are quite different from those of esters, it is to be expected that solvent and substituent variation will have different effects upon the n → π* transition of acids than upon this transition of esters. In order to examine these effects, we have undertaken the measurement of the spectra of a number of carboxylic acids and their esters in three different solvents. These solvents were *n*-hexane, as a representative nonpolar solvent, acetonitrile, as a representative polar aprotic solvent, and water, as a representative polar hydrogen-bonding solvent. With supplies of these carboxylic acids and their esters available, it was also convenient to examine the spectra of these compounds as neat liquids, in the region of the shoulder described by Hartleb.[9]

Results and Discussion

The near-ultraviolet absorption spectra of 13 aliphatic carboxylic acids (Table I), 13 ethyl esters (Table II), and 16 alkyl acetates (Table III) were determined for solutions in *n*-hexane, acetonitrile, and water, and for neat liquids. All of the measurements were made with the samples thermostated at 20.0 °C,[10] in 1-cm rectangular cells. The wavelengths of the peaks, λ_{max}, were reproducible within ±0.3 nm; and the molar absorptivities, ϵ_{max}, of these peaks for the solution spectra were reproducible within ±8. Since the excitation energies are proportional to the wavenumbers of the peaks, $\bar{\nu}_{max}$, these latter values expressed in kilokaysers have been calculated, and are recorded in the tables.