1050, 749, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (t, 3, J = 7.0 Hz, CH_3), 2.07 (d, d, 2, J = 6.6 Hz, CH_2), 3.35 (s, 3, CH_3O), 3.55 (s, 3, CH_3O), 3.67 (q, 2, J = 7.0 Hz, CH_2O), 4.73 (t, 1, J = 6.6 Hz, S-CH-O), 4.80 (t, 1, J = 7.3 Hz, O-CH-O), 7.28-7.80 (m, 5, S-Ph).

Anal. Calcd for $C_{13}H_{20}O_3S$: C, 60.92; H, 7.87. Found: C, 61.12; H, 8.11.

2-[Methoxy(phenylthio)methyl]cycloheptanone (5, $R^1 = R^2 = -(CH_2)_5-$): bp 67-69 °C (0.005 mm); IR (neat) 3057, 2825, 1706, 1584, 1476, 1096, 747, 690 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.87-2.77 (m, 11, CH_2, CH), 3.35-3.42 (m, 3, CH_3O), 4.83-5.11 (m, 1, O-CH-S), 7.19-7.65 (m, 5, S-Ph).

Anal. Calcd for $C_{15}H_{20}O_2S$: C, 68.16; H, 7.63. Found: C, 68.21; H, 7.70.

2-[Methoxy (phenylthio)methyl]cyclododecanone (5, $R^1 = R^2 = -(CH_2)_{10}-$): bp 97-99 °C (0.005 mm); IR (neat) 3049, 2815, 1710, 1582, 1471, 1443, 1090, 741, 717, 691 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.05-2.00 (br, 18, CH_2), 2.25-2.80 (m, 3, CH_2, CH), 3.40 (s, 3, CH_3O), 4.54 (d, 1, J = 9.5 Hz, S-CH-O), 7.13-7.55 (m, 5, S-Ph); ^{13}C NMR ($CDCl_3$) δ 21.61 (t), 22.08 (t), 22.37 (t), 23.84 (t), 24.13 (t), 26.01 (t), 26.30 (t), 27.42 (t), 38.81 (t), 55.77 (d, C-12), 56.30 (q, C-18), 91.76 (d, C-13), 128.00 (d, C-17), 128.75 (d, C-15), 131.75 (d, C-16), 134.15 (s, C-14), 211.71 (s, C-1).

Anal. Calcd for $C_{20}H_{30}O_2S$: C, 71.82; H, 9.04. Found: C, 71.72; H, 9.08.

2-Methoxy-3-[methoxy(phenylthio)methyl]tetrahydropyran (5, $R^1 = R^2 = -(CH_2)_3O-$): bp 54-56 °C (0.005 mm); IR (neat) 3025, 1586, 1438, 1180, 1109, 1076, 961, 752, 688 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.10-2.10 (m, 5, CH_2, CH), 3.21-3.50 (m, 8, CH_3O, CH_2O), 4.18-4.90 (m, 2, CH), 7.05-7.60 (m, 5, S-Ph).

Anal. Calcd for $C_{14}H_{20}O_3S$: C, 62.67; H, 7.51. Found: C, 62.53; H, 7.55.

Methyl 7-Chloro-7-(phenylthio)-6-heptenoate (9). Electrolysis of 8 was carried out in the same manner as described above to give **9** in 40% yield: bp 73-75 °C (0.002 mm); IR (neat) 3039, 2852, 1735, 1585, 1480, 1442, 1205, 1170, 1020, 740, 686 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.16-2.00 (m, 4, CH_2), 2.00-2.59 (m, 4, CH_2), 3.67 (s, 3, CH_3O), 6.21 (t, 1, J = 7.8 Hz, HC=C), 7.11-7.47 (br s, 5, S-Ph).

Anal. Calcd for $C_{14}H_{17}ClO_2S$: C, 59.03; H, 6.02. Found: C, 59.11; H, 6.21.

3-(Phenylthio)-1,1,3-trimethoxypropane (6b, $R^1 = R^2 = H$; Y = OMe). A solution of 4 ($R^1 = R^2 = H$, Y = OEt, 70 mg, 0.36 mmol) and p-$CH_3C_6H_4SO_3NEt_4$ (2 g) in dry MeOH (40 mL) was charged in the anode compartment. A solution of p-$CH_3C_6H_4SO_3NEt_4$ (1 g) in dry MeOH (20 mL) was poured into the cathode compartment. The mixture was electrolyzed under a constant applied voltage of 3 V at a current of 1.20-1.33 mA/cm^2 at 20-30 °C. After passage of 2.3 F/mol of electricity, the anode solution was concentrated and the residue was taken up in ether. The extracts were washed with brine, dried (Na_2SO_4), and concentrated. The crude product was chromatographed (SiO_2, hexane-ether 40:1) to give 63 mg (72%) of **6b** ($R^1 = R^2 = H$, Y = OMe) along with 5.5 mg (18%) of diphenyl disulfide, **6b:** IR (neat) 3040, 1588, 1477, 1440, 1130, 1080, 1028, 972, 750, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.02 (t, 2, J = 6.5 Hz, CH_2), 3.31 (s, 6, CH_3O), 3.50 (s, 3, CH_3O), 4.56 (t, 1, J = 6.5 Hz, O-CH-O), 4.70 (t, 1, J = 6.5 Hz, O-CH-S), 7.13-7.59 (m, 5, S-Ph).

Anal. Calcd for $C_{12}H_{18}O_3S$: C, 59.49; H, 7.49. Found: C, 59.40; H, 7.55.

Registry No.—**6b** ($R^1 = R^2 = H$; Y = OMe), 68002-06-2; **8**, 68002-07-3; **9**, 68002-08-4; 1-methoxy-1-cyclohexene, 931-57-7; phenylthiomethyl chloride, 7205-91-6; 1-ethoxyethylene, 109-92-2; 1-methoxy-1-cyclododecane, 32400-32-1.

References and Notes

(1) S. Torii, T. Okamoto, and N. Ueno, *Chem. Commun.*, 293 (1978).
(2) M. Klehr and H. J. Schäfer, *Angew. Chem., Int. Ed. Engl.*, **14**, 247 (1975).
(3) U. Schöllkopf, G. J. Lehmann, J. Paust, and H.-D. Härtl, *Chem. Ber.*, **97**, 1527 (1964); G. Boche and D. R. Schneider, *Tetrahedron Lett.*, 4247 (1975).
(4) Synthetic utilities of the alkoxy(alkylthio)methyl group have been reported: B. M. Trost and C. H. Miller, *J. Am. Chem. Soc.*, **97**, 7182 (1975).
(5) The considerably lower oxidation potential of **4** ($R^1 = R^2 = -(CH_2)_4-$), compared to those of phenyl sulfide derivatives (1.45 V vs. SCE: S. Torii, K. Uneyama, K. Iida, and K. Sasaki, *Tetrahedron Lett.*, 4513 (1972)) and alkoxycyclopropane (1.64 V vs. SCE),[2] reveals that the contribution of the electron-donating groups such as both phenylthio and alkoxy functions attached to the cyclopropane ring would cause the suppression of the oxidation potential of **4**.
(6) K. Uneyama and S. Torii, *Tetrahedron Lett.*, 329 (1971).
(7) Sulfur-stabilized cation has been discussed: (a) B. M. Trost and Y. Tamaru, *J. Am. Chem. Soc.*, **97**, 3528 (1975); (b) B. M. Trost and K. Hiroi, *ibid.*, **98**, 4313 (1976).
(8) R. A. Wohl, *Synthesis*, 38 (1974).
(9) B. M. Trost and R. A. Kunz, *J. Org. Chem.*, **39**, 2648 (1974).
(10) M. Saquet, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **275**, 283 (1972).
(11) U. Schöllkopf, F. P. Woerner, and E. Wiskott, *Chem. Ber.*, **99**, 806 (1966).

Facile Synthesis of Triimidazo[1,3,5]triazine Derivatives

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During the preparation of 1-alkyl-4-methoxy-5,5-dimethyl-2-imidazolidinones **2** (X = O)[2] by reaction of α-chloroaldimines **1** with potassium cyanate in methanol, small amounts of high-melting side products were isolated. It was assumed that these compounds were directly derived from the methoxyimidazolidinones **2** (X = O) and not from a further reaction of the imidazolidinones with potassium cyanate. We now describe the synthesis and structural determination of these byproducts.

Heating of 1-alkyl-4-methoxy-5,5-dimethyl-2-imidazolidinones **2** (X = O) at 150 °C in vacuo afforded the same compounds in high yields (Table I). In all cases only one isomer was obtained by crystallization. Even in the mother liquor no isomeric compound was detectable (vide infra). The structure elucidation was obtained by X-ray diffraction studies on the *tert*-butyl compound. The structure was shown to be 3,7,11-tri-*tert*-butyl-4,4,8,8,12,12,-hexamethyl-1*H*,2*H*,5*H*,6*H*,9*H*,10*H*-triimidazo[3,4-*a*;3′,4′-*c*;3″,4″-*e*]-[1,3,5]triazine-2,6,10-trione (**5d**). The compound crystallized in the monoclinic space group $P2_1$ with $Z = 2$, $a = 11.184$ (5), $b = 10.148$ (7), $c = 13.746$ (5) Å, and $\beta = 106.49$ (3)°. The molecular structure and the ORTEP drawing are given in Figure 1. The atom numbering system used, the positional and thermal parameters, the intramolecular bond distances, the valence angles, and the torsional angles are listed in tables included in the microfilm edition of this journal. The formation of the hexahydro[1,3,5]triazines can be explained by loss of methanol from the 4-methoxy-2-imidazolidinones **2** on heating to give the intermediate 2-imidazolidinones **4** (X = O) which rapidly trimerized into **5.** An analogous elimination of methanol has been observed during the in situ preparation of 1-phenyl-3-imidazolin-2,5-diones from 5-methoxy-3-phenylhydantoines.[3,4]

Other trimerizations of imino compounds have been reported in the case of 3,4-diazanorcaradiene,[5] β,β-dimethylindolenine,[6] (2-chloro-2-methylpropylidene)imine[7] and the dehydrohalogenation of *N*-chloropiperidine.[8,9] In our case compounds **4** (X = O) trimerized very rapidly due to activation of an additional carbonyl group on the nitrogen of the imino function. It is known that *N*-acylimines rapidly undergo nucleophilic addition at the activated carbon–nitrogen double bond.[10]

The corresponding thione compounds **6** were obtained in the same way from the 1-alkyl-5,5-dimethyl-4-methoxy-2-imidazolidinethiones **3**,[11] except when R = *t*-Bu. Compound **3** (R = *t*-Bu) did not lose methanol even on prolonged heating at 200 °C.

The structure of compounds **5** and **6** was further confirmed

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Table I. Synthesis of Triimidazo[1,3,5]triazines 5 and 6

	registry no.	X	R	yield, %	mp, °C	formula[a]
5a	67969-48-6	O	Me	56	>300	$C_{18}H_{30}N_6O_3$
5b	67969-49-7	O	Et	67	157	$C_{21}H_{36}N_6O_3$
5c	67969-50-0	O	*i*-Pr	89	216	$C_{24}H_{42}N_6O_3$
5d	67969-51-1	O	*t*-Bu	84	224	$C_{27}H_{48}N_6O_3$
5e	67969-52-2	O	cyclohexyl	79	>300	$C_{33}H_{54}N_6O_3$
6c	67969-53-3	S	*i*-Pr	74	250	$C_{24}H_{42}N_6S_3$
6e	67969-54-4	S	cyclohexyl	81	>300	$C_{33}H_{54}N_6S_3$

[a] Compounds **5** and **6** gave satisfactory analytical data: C, H, N analyses were obtained for **5a, 5c, 5d,** and **6c,** while N analyses were obtained for **5b, 5e,** and **6e.**

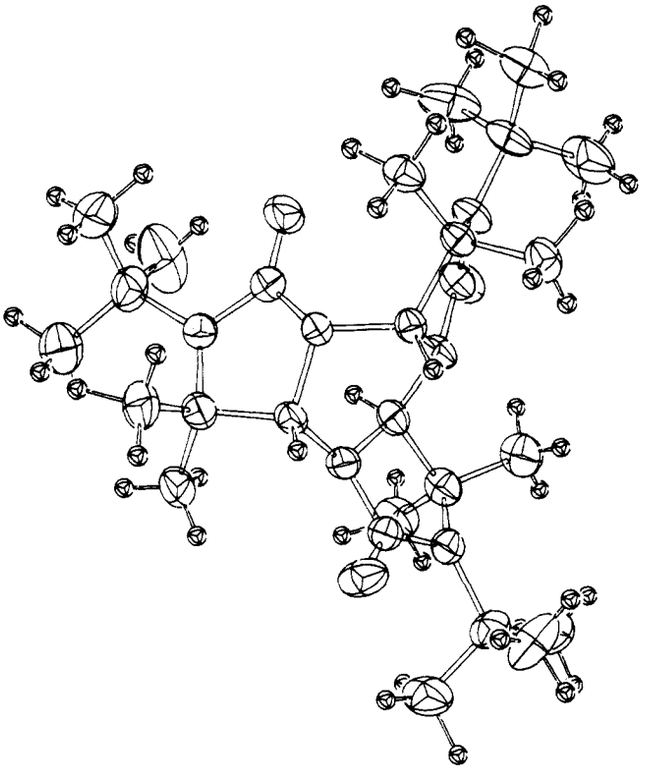


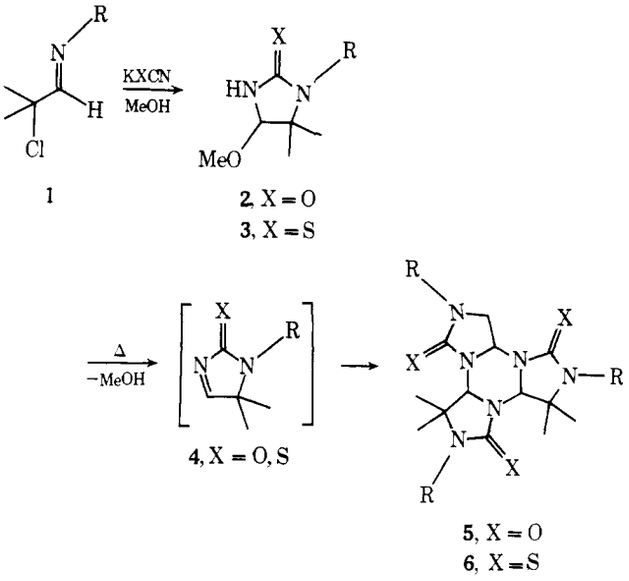
Figure 1. ORTEP drawing of triimidazo[1,3,5]triazine derivative **5d.**

by mass spectrometry. The mass spectra showed the $M^{\cdot+}$ of the hexahydrotriazines next to the $M^{\cdot+} + 1$ and the $M^{\cdot+}$ of **4** as important ions (except when R = cyclohexyl).

A number of features in the NMR spectrum of **5** and **6** could be assigned to structural facets. The three protons of the hexahydro[1,3,5]triazine ring were observed as three singlets (each integrating for one hydrogen) at approximately δ 4.0, 4.6, and 5.2 for **5** and δ 4.2, 5.3, and 6.3 for **6**. Thus the trimers **5** and **6** must have such a structure in which the hexahydro[1,3,5]triazine protons experienced a completely different anisotropic effect of the carbonyl or thiocarbonyl function. In addition one of the six geminal methyl groups was found at a higher δ value (±0.3 ppm), a phenomenon which was also noticed in the case of the trimer derived from β,β-dimethylindolenine.[6]

In the ^{13}C NMR spectrum of **5d** the C atoms of the three carbonyl functions had a different chemical shift, while also the chemical shifts of the triazine C atoms were readily distinguishable. From the X-ray crystallographic analysis (see ORTEP drawing in Figure 1) it was concluded that compound **5d** exhibited an asymmetric structure (C_1 point group). The compound existed as a racemic mixture of RRS and SSR isomers. These results fitted very well with the observed NMR data (^1H and ^{13}C). As pointed out above, it is stressed that in

Scheme I

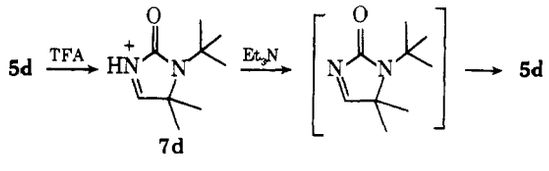


all cases no other isomer than the asymmetric one was detected. These findings are deviating from previously observed trimerizations of appropriate imino compounds. For instance, piperideine has been found to trimerize into a dissymmetric (C_3 symmetry) and an asymmetric (C_1 point group) compound (besides a third compound, i.e., isotripiperideine, without hexahydro[1,3,5]triazine structure).[8,9] Recording the NMR spectrum of **5d** in $CDCl_3$/TFA (3:1) showed the spectrum of the imidazolinium salt **7d.** The signals of the three different methine protons disappeared and one signal was observed for the methyls (δ 1.56), so all the C-methyl groups must be equivalent. The azomethinium proton was found at δ 9.30. Treatment of **7d** with triethylamine resulted in liberation of the monomer **4d** (X = O) which unfortunately could not be isolated an a preparative scale but was detected by GLC–MS coupling. The stereoview as revealed by the X-ray analysis established a boat-like conformation but no definite conclusion concerning the conformation in solution can be drawn.

Experimental Section

General. Infrared spectra were measured with a Perkin-Elmer Model 257 spectrometer. ^1H NMR spectra were obtained on a Varian T-60 spectrometer. Proton noise decoupled ^{13}C NMR spectra were recorded with a Varian FT-80 apparatus at 20 MHz. Mass spectra

Scheme II



were obtained from A.E.I. MS 30 or A.E.I. MS 50 mass spectrometers (70 eV). GS–MS couplings were performed by means of a Pye-Unicam gas chromatograph (SE 30, 3%, 1.5 m) coupled with a A.E.I. MS 20 spectrometer. Compounds **2** and **3** were prepared as previously described.[2,11] Melting points were measured with a Kofler hot stage and were uncorrected.

Preparation of Triimidazo[1,3,5]triazine Derivatives 5 and 6. In a typical experiment, 5.0 g (0.025 mol) of 1-*tert*-butyl-5,5-dimethyl-4-methoxy-2-imidazolidinone (**2d**) was heated at 140 °C in vacuo (0.05 mm Hg) for 15 min. After cooling the crude product was dissolved in 50 mL of ether and filtered. The filtrate was concentrated and triturated with hexane. After standing overnight at −5 °C the crystals were isolated by filtration and washed with cold hexane. Recrystallization was performed from hexane. There was obtained 3.5 g of 3,7,11-tri-*tert*-butyl-4,4,8,8,12,12-hexamethyl-1*H*,2*H*,5*H*,6*H*,9*H*,10*H*-triimidazo[3,4-*a*;3′,4′-*c*;3″,4″-*e*][1,3,5]triazine-2,6,10-trione (**5d**) (yield 84%): mp 224 °C; NMR ($CDCl_3$) 1.41 (18 H, s,), 1.48 (21 H, s), 1.53 (3 H, s), 1.72 (3 H, s) (all these singlets are due to resonances of N–*t*-Bu and $C(CH_3)_2$), 3.76 (1 H, s), 4.52 (1 H, s), 5.00 (1 H, s) (the latter three singlets are resonances of N–CH–N).

^{13}C NMR ($CDCl_3$). The δ values (ppm) of **5d** are given (noise decoupled); the multiplicities, given between brackets, were obtained from the off-resonance decoupled spectrum: 23.7, 25.9, 26.2, 26.9, 29.3, 29.3, 29.4, 29.8, 29.8, 29.8 (t), 55.5 (s), 56.0 (s), 56.1 (s) (N–C); 61.0 (s), 61.1 (s), 64.0 (s) (N–C); 72.5 (d), 75.8 (d), 77.5 (d) (N–C–N); 158.2 (s), 159.4 (s), 160.1 (s) (C=O). IR (KBr) 1715 and 1695 cm^{-1} ($\nu_{C=O}$). Mass spectrum *m/e* (relative abundance): 504 (M^+, 6), 490 (29), 489 (100), 447 (10), 405 (17), 337 (19), 336 (15), 321 (20), 279 (34), 237 (18), 223 (19), 169 (65), 168 (8), 167 (10), 153 (15), 124 (22), 113 (53), 102 (15), 98 (10), 84 (14), 70 (15), 58 (17), 57 (38), 42 (15), 41 (24).

X-ray Crystallographic Analysis of 5d. The data were collected on a Syntex $P2_1$ diffractometer. Experimental conditions: source Mo K$\bar{\alpha}$, $2\theta_{max} = 47°$; total number of independent reflections 2347; total observed reflections 2035. The structure was determined by direct methods using the MULTAN 77 program[12] and refined with the X-ray 72 system[13] to an *R* value of 4.1%.

Attempted Preparation of 1-*tert*-Butyl-5,5-dimethyl-2-imidazolinone (4d) (X = O, R = *t*-Bu). A solution of 0.5 g of **5d** in 10 mL of chloroform was treated with 1 mL of TFA. After standing for 15 min the reaction mixture was treated with an excess of triethylamine. GLC–MS provided the mass spectrum of **4d** (X = O, R = *t*-Bu): *m/e* 168 (M^+, 14), 153 (50), 113 (29), 112 (14), 97 (16), 84 (22), 70 (24), 58 (100), 42 (29), 41 (64).

However, usual workup resulted in trimerization into **5d.**

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Registry No.—**2a,** 67969-55-5; **2b,** 67969-56-6; **2c,** 64942-53-6; **2d,** 64942-51-4; **2e,** 64942-52-5; **3c,** 63547-71-7; **3e,** 63547-69-3; **4d,** 67969-57-7; **7d,** 67969-58-8.

Supplementary Material Available: atom numbering system used, Figure 2; full spectrometric data (IR, NMR, MS) of triimidazo[1,3,5]triazines **5** and **6**, Table II; positional and thermal parameters, Table III; intramolecular bond distances, Table IV; and valence angles and torsional angles, Tables V and VI (11 pages). Ordering information is given on any current masthead page.

References and Notes

(1) N. De Kimpe and J. P. Declercq, "Aangesteld Navorser" of the Belgian "Nationaal Fonds voor Wetenschappelijk Onderzoek".
(2) N. De Kimpe, R. Verhé, L. De Buyck, and N. Schamp, *Bull. Soc. Chim. Belg.*, **86,** 663 (1977).
(3) D. Ben-Ishai and E. Goldstein, *Tetrahedron*, **27,** 3119 (1971), and references cited therein; see also: W. Armarego and S. Sharma; *J. Chem. Soc. C*, 1600 (1970).
(4) D. Kim and S. M. Weinreb, *J. Org. Chem.*, **43,** 121 (1978).
(5) G. Maier and T. Sayrac, *Chem. Ber.*, **101,** 1354 (1968).
(6) H. Fritz and P. Pfaender, *Chem. Ber.*, **98,** 989 (1965).
(7) A. Kirrmann and H. I. Joschek, *Bull. Soc. Chim. Fr.*, 2483 (1963).
(8) C. Schöpf, A. Komzak, F. Braunn, and E. Jacobi, *Justus Liebigs Ann. Chem.*, **559,** 1 (1948); C. Schöpf, H. Arm, and H. Krimm, *Chem. Ber.*, **84,** 690 (1951); C. Schöpf, H. Arm, and F. Braun, *Chem. Ber.*, **85,** 937 (1952).
(9) H. Kessler, H. Möhrle, and G. Zimmermann, *J. Org. Chem.*, **42,** 66 (1977).
(10) N. De Kimpe, R. Verhé, L. De Buyck, W. Dejonghe, and N. Schamp, *Bull. Soc. Chim. Belg.*, **85,** 763 (1976).
(11) N. De Kimpe, R. Verhé, L. De Buyck, N. Schamp, J. P. Declercq, G. Germain, and M. Van Meersche, *J. Org. Chem.*, **42,** 3704 (1977).
(12) P. Main, L. Lessinger, M. M. Woolfson, G. Germain, and J. P. Declercq, "Multan 77, A System of Computer Programmes for the Automatic Solution of Crystal Structures from X-ray Diffraction Data", York (U.K.) and Louvain-La-Neuve (Belgium), 1977.
(13) J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall; "X-ray 72 System", Technical Report TR-192, Computer Science Center, University of Maryland, 1972.

Communications

Aryl Effects and Acidities of Ammonia, Toluene, and Methane in Dipolar Nonhydroxylic Solvents

Summary: For a series of carbon acids, $ArCH_2G$ and $ArCH(CN)_2$, with G = C_6H_5, CN, $COCH_3$, and NO_2, the equilibrium acidities in Me_2SO reveal a linear correlation between the Hammett ρ and the size of the Ph effect (ΔpK for Ar = Ph vs. Ar = H or Me).

Sir: In an earlier paper[1] we showed that, for a series of carbon acids where steric effects are not expected to be of major importance, the position of equilibrium 1 shifted progressively to the left as the parent $MeCH_2G$ acid was made stronger by changing the nature of G. (For example, as G was changed from CN to COR to NO_2, the α-Ph acidifying effect decreased progressively from 10.6 to 7.3 to 4.5 p*K* units.[1]) This was attributed to resonance saturation of the Ph effect.[2] That is, progressively greater delocalization of the negative charge to G in the stronger acids caused a progressive decrease in the charge density α to Ph, resulting in a progressively smaller Ph effect.

$$PhCH_2G + MeCHG^- \overset{Me_2SO}{\rightleftharpoons} PhCHG^- + MeCH_2G \quad (1)$$

Since smaller Ph effects are associated with greater charge delocalization into G and with consequent lesser charge delocalization into the phenyl ring, we can expect the size of the Hammett ρ to decrease with an increase in the acidity of the parent acid, $PhCH_2G$. In other words, ρ should also decrease as G is changed from CN to COR to NO_2, as is observed (Table I).

Examination of Table I shows that the size of the α-Ph effect usually decreases as the acidity of the parent acid increases, but that the two are not linearly related. The structural change from $CH_3C_6H_5$ to CH_3CN increases the acidity by over 10 p*K* units, but the decrease in the size of the α-Ph effect is six times smaller than for the change from CH_3CN to CH_3COCH_3, where only a 4.5 p*K* unit increase in acidity occurs. These results, together with the large α-Ph effect for $CH_2(CN)_2$ and the large ρ for the $ArCH(CN)_2$ system, appear to be associated with a relatively low ratio of resonance to polar effect for the cyano group in stabilizing an α-carbanion.[4]