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–C**H**–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**.

Acknowledgments. We are indebted to Dr. C. Van de Sande (Laboratory for Organic Synthesis, Faculty of Sciences, State University of Gent) for recording the mass spectra. We also thank Dr. F. Borremans and Dr. R. Callens (Laboratory of NMR spectrometry, Faculty of Sciences, State University of Gent) for helpful discussions regarding the NMR spectra. Furthermore, the "National Fonds voor Wetenschappelijk Onderzoek" is gratefully acknowledged for financial support to the laboratory.

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]

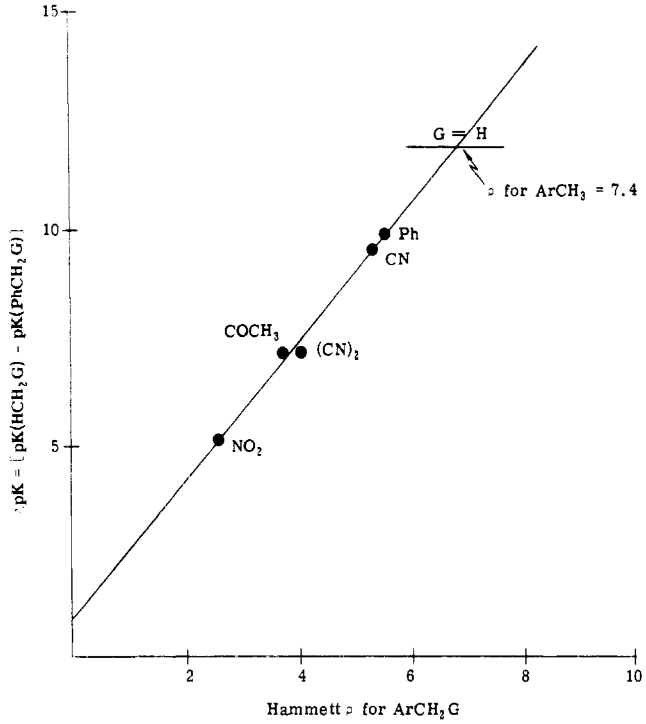


Figure 1. Plot of ΔpKs, derived from absolute equilibrium acidities in Me_2SO, for HCH_2G vs. $PhCH_2G$ against the Hammett ρ for $ArCH_2G$.

In other words, there is a much higher negative charge density on the α-carbon atom in CH_2CN^- and $CH(CN)_2^-$ anions than would be anticipated from the acidities of the parent acids. This results in enhanced α-Ph effects and ρ values for these systems (Table I). Note in this respect that the Ph effect and ρ value for the $CH_2(CN)_2$ parent acid are comparable in size to those for the CH_3COCH_3 parent acid, despite the fact that the latter parent acid has a 15.7 unit higher p*K*. The much larger ratio of resonance to polar effect for the CH_3CO group vs. the CN group explains the near equivalence of the Ph effects and ρ values in these systems.

A plot of the Ph effects and ρ values for the five systems represented in Table I is linear (Figure 1: $R^2 = 0.99$;[6] slope = 1.6 ± 0.09[7]). When ρ values for other $ArCH_2G$ (or like) systems can be determined or estimated it is possible to use the line in Figure 1 to estimate the size of the Ph effect and then to estimate the acidity of the corresponding HCH_2G parent acid from that of $PhCH_2G$. We have applied this analysis to estimate p*K*s of H_2O, NH_3, and CH_4. For ArOH $\rho = 5.6$,[8] and the Ph effect derived from the line in Figure 1 is 10. This figure can be combined with the p*K* of 18.0 for PhOH[8] to give an estimated p*K* of HOH of 28 in Me_2SO.[9] The experimental value is 31.4.[8] Similarly, for $ArNH_2$ $\rho = 5.67$,[5] which leads to a Ph effect of 10. This combined with the p*K* of $PhNH_2$ of 30.7 gives an estimated p*K* for NH_3 of 40.7 in Me_2SO.[10] Finally, for $ArCH_3$ an estimated $\rho = 7.4$[12] gives a Ph effect of 13, which, when combined with the p*K* of 42 for toluene derived earlier,[5] gives an estimated p*K* of 55 for methane.

Minimum p*K*s for toluene and methane can be derived from the following extrapolations. (The cyano function is chosen because of its low steric demands.)

$$\begin{array}{ccccc} PhCH(CN)_2 & \xrightarrow{\Delta pK\ =\ 17.7} & PhCH_2CN & \xrightarrow{(+17.7)} & PhCH_3 \\ pK\ 4.2 & & pK\ 21.9 & & (pK\ 39.6) \\ CH_2(CN)_2 & \xrightarrow{\Delta pK\ =\ 20} & CH_3CN & \xrightarrow{(+20)} & CH_4 \\ pK\ 11.1 & & pK\ 31.1 & & (pK\ 51.1) \end{array}$$

The extrapolated values are minimal, since they assume the same Δp*K* for each CN effect and thus fail to take into account the resonance saturation effect. In the gas phase in the series $CH_4 \rightarrow CH_3CN \rightarrow CH_2(CN)_2$ the effect of substituting the second CN group for H is 20% smaller than for the first due to the resonance saturation effect.[13] If we assume a similar saturation effect in Me_2SO, the increment from CH_3CN to CH_4 would be 20% larger than indicated, leading to a p*K* of about 55 for methane.

Table I. α-Phenyl Effects and Hammett Substituent Effects on Equilibrium Acidities in Dimethyl Sulfoxide Solution

parent acid	p*K*	α-Ph effect[a]	Hammett ρ[b]
$CH_3C_6H_5$	42[c]	10	5.7[d]
CH_3CN	31.3	9.6	5.5[d]
CH_3COCH_3	26.5	7.2	3.9[e]
CH_3NO_2	17.2	5.2	2.7[f]
$CH_2(CN)_2$	11.1	7.2	4.1[g]

[a] $\Delta pK = [pK(CH_3G) - pK(PhCH_2G)]$ (statistically corrected for the number of acidic hydrogen atoms). [b] ρ for $ArCH_2G$. [c] Estimated from an extrapolation, see ref 5. [d] J. E. Bares, Ph.D. Dissertation, Northwestern University, 1976. [e] R. J. McCallum and U. E. Wiersum, unpublished results. [f] W. S. Matthews, unpublished results. [g] J. C. Branca, Ph.D. Dissertation, Northwestern University, 1979.

Our estimate of p*K* 42 for toluene in a dipolar nonhydroxylic solvent is in good agreement with the ion pair p*K* of 41 estimated in cyclohexylamine,[14] but is in poor agreement with the "p*K*" of 54 for toluene determined by the electrochemical method;[15,16] our p*K* of 55 for methane is also much lower than the 68–70 obtained for methane.[15,16]

Acknowledgment is made to the National Science Foundation for support of this work. We also wish to express our appreciation to the Chemical Products Division of Crown Zellerbach, Camas, Washington, for a generous gift of Me_2SO.

References and Notes

(1) F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. J. McCollum, M. Van Der Puy, N. R. Vanier, and W. S. Matthews, *J. Org. Chem.*, **42,** 321 (1977).

(2) The principle of resonance saturation has been recognized for many years, but examples unperturbed by steric effects are relatively rare.[3]

(3) (a) F. G. Bordwell and G. J. McCollum, *J. Org. Chem.*, **41,** 2391 (1976); (b) F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. E. Drucker, J. Gerhold, G. J. McCollum, M. Van Der Puy, N. R. Vanier, and W. S. Matthews, *ibid.*, **42,** 326 (1977).

(4) A low resonance to polar ratio for the effect of the CN group, relative to the effects of C_6H_5 and COR groups, is clear from previous data.[1] It seems likely from the data in Table I that the NO_2 group, like the C_6H_5 and COR groups, has a relatively high resonance to polar ratio.

(5) F. G. Bordwell, D. Algrim, and N. R. Vanier, *J. Org. Chem.*, **42,** 1617 (1977).

(6) R^2, the square of the correlation coefficient, r, is a measure of precision. It is that fraction of the total variance of the phenyl effect that is explained by linear regression analysis. See R. J. McCallum, *J. Chem. Educ.*, submitted for publication.

(7) The standard deviation: the standard deviation at the 95% confidence level [see W. H. Davis, Jr. and W. A. Pryor, *J. Chem. Educ.*, **43,** 285 (1976)] is threefold higher, partly because we have only five points.

(8) W. N. Olmstead, unpublished results.

(9) One can argue that replacement of Me by Ph, as in eq 1, provides a better model for the Ph effect than replacing H by Ph.[1] The Ph effects calculated in this way, using known or estimated p*K*s for the parent $MeCH_2G$ acids, also gave a linear plot with ρ ($R^2 = 0.93$; slope = 1.8 ± 0.3[7]). Using this plot the estimated p*K* of MeOH is 28, which compares well with the observed value of 29.0.[8]

(10) Two other estimates of the p*K* of ammonia give values of comparable magnitude. In liquid ammonia at −33 °C the difference in acidities of NH_3 and $C_6H_5NH_2$ is about 11 p*K* units.[11] Assuming that the Δp*K* for $C_6H_5NH_2$ vs. NH_3 observed in liquid NH_3 holds also in Me_2SO places the p*K* of NH_3 in Me_2SO at about 43. A plot of p*K*s of $ArNH_2$ in Me_2SO vs. p*K*s of $ArNH_3^+$ in H_2O is linear ($R^2 = 0.99$; slope = 1.84 ± 0.06). By placing the p*K* of NH_4^+ in H_2O (p*K* 9.27) on this plot a p*K* of 39 is estimated for NH_3. The best estimate is probably an average of these three values, i.e., 41.

(11) J. H. Takemoto and J. J. Lagowski, *J. Am. Chem. Soc.*, **91,** 3785 (1969); J. J. Lagowski, *Pure Appl. Chem.*, **25,** 429 (1971).

(12) For $ArCH(CN)_2$ $\rho_{meta} = 4.1$ and for $ArCH_2CN$ $\rho_{meta} = 5.5$. Assuming a similar incremental increase between $arCH_2CN$ and $ArCH_3$ leads to a $\rho_{meta} = 7.4$ for $ArCH_3$.

(13) J. E. Bartmess and R. T. McIver, Jr., unpublished data privately communicated.

(14) A. Streitwieser, Jr., J. R. Murdoch, G. Häfelinger, and C. J. Chang, *J. Am.*

Chem. Soc., **95**, 4248 (1973); A. Streitwieser, Jr. and F. Guibé, *ibid.*, **100**, 4532 (1978).

(15) R. Breslow and J. L. Grant, *J. Am. Chem. Soc.*, **99**, 7745 (1977).

(16) The "p*K*s" obtained by the electrochemical method are *relative* numbers. Although these p*K*s (in acetonitrile) are based on an arbitrary reference standard [the ion pair p*K* of triphenylmethane in cyclohexylamine (CHA) solution] a rough comparison with p*K*s in Me$_2$SO, which are based on an absolute standard (direct measurements in the low p*K* region), can be made because the p*K* of triphenylmethane in Me$_2$SO (30.6[17]) is close to its ion pair p*K* in CHA (31.5[14]) and because relative p*K*s *for acids forming delocalized anions do not differ much with medium.*[17]

(17) W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, R. J. McCallum, G. J. McCollum, and N. R. Vanier, *J. Am. Chem. Soc.*, **97**, 7006 (1975).

Donald Algrim, Joseph E. Bares
John C. Branca, F. G. Bordwell*
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

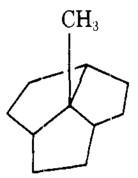
Received July 31, 1978

Additions and Corrections

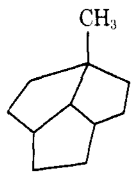
Vol. 40, 1975

Naotake Takaishi, Yoshiaki Inamoto,* Kiyoshi Tsuchihashi, Kazuaki Yashima, and Koji Aigami: Identification of Intermediates in the Trifluoromethanesulfonic Acid Catalyzed Adamantane Rearrangement of 2,3-*endo*- and -*exo*-Tetramethylenenorbornane.

Page 2930. Chart I. Structures **10** (A_1) and **11** (A_3) should be:



10
(A_1)



11
(A_3)

Page 2932. Table II. ^{13}C NMR signals should be read as:

compd		
notation as unknown	structure	^{13}C NMR signals, ppm (multiplicity, rel intensity)
A_2	4	24.8 (t, 3), 40.5 (t, 6), 60.4 (s, 0.9)
A_1	10	28.4 (q, 1), 31.8 (t, 6), 52.8 (d, 3), 62.8 (s, 0.3)
A_3	11	27.8 (q, 1), 31.7 (t, 4), 39.4 (t, 2), 45.5 (d, 2), 51.4 (s, 0.3), 61.7 (d, 1)

Slayton A. Evans* and Andrew L. Ternay, Jr.*: Preferred Conformer Assignments of Diaryl Sulfoxides Employing Aromatic Solvent Induced Shifts.

Page 2294. Experimental Section. Syntheses labeled *cis*-9-ethylthioxanthene *S*-oxide (*cis*-**5**) and *cis*-9-isopropylthioxanthene *S*-oxide (*cis*-**6**) should be relabeled trans. Syntheses labeled *trans*-9-ethylthioxanthene *S*-oxide (*trans*-**5**) and *trans*-9-isopropylthioxanthene *S*-oxide (*trans*-**6**) should be relabeled cis. Table I is correct. (We thank Professor Y. Tamura for noting this exchange.)

Werner Herz* and Ram P. Sharma: A *trans*-1,2-*cis*-4,5-Germacradienolide and Other New Germacradienolides from *Tithonia* Species.

Page 3122. Column 1, lines 24–25 should read: The CD curve of **1a** exhibits a positive Cotton effect while that of **4a** is negative, although no change has occurred . . .

Vol. 41, 1976

Courtland Symmes, Jr., and Louis D. Quin*: 1-Vinylcycloalkenes in the McCormack Cycloaddition with Phosphonous Dihalides. Stereochemistry of Some Resulting Bicyclic Phospholene Oxides.

Page 242. The ^{31}P NMR shifts on line 26 are reversed; the entry should read: δ +28.6 (**13a**, 56%) and +26.2 (**13b**, 44%).

K. Grant Taylor* and Melvin S. Clark, Jr.: Aliphatic Azoxy Compounds. 5. Functionalization of (*Z*)-Phenylmethyldiazene 1-Oxide.

Page 1145. Column 1, line 7 from bottom: "(ϵ 1900)" should be "(ϵ 11 900)".

D. C. Baker, J. Defaye, A. Gadelle, and D. Horton*: Reduction of Ketones with Incorporation of Deuterium at the α Position: Anomalous Reduction of Keto Sugar Derivatives.

Page 3836. Table I. The data for compound **9** should read: **9**, CDCl$_3^e$, 4.95 d (H-1), 4.79 dd (H-2), 4.15 t (H-3), 3.52 t (H-4), 3.84 sx (H-5), 4.29 q (H-6), 3.74 t (H-6′), 5.53 s (PhCH), 2.12 s (OAc), 3.39 s (OMe), 7.40 m (aryl).

Page 3837. Table II. The data for compound **9** should read: **9**, CDCl$_3^e$, 3.7 ($J_{1,2}$), 9.5 ($J_{2,3}$), 9.5 ($J_{3,4}$), 9.5 ($J_{4,5}$), 4.0 ($J_{5,6}$), 10 ($J_{5,6'}$), 9.5 ($J_{6,6'}$).

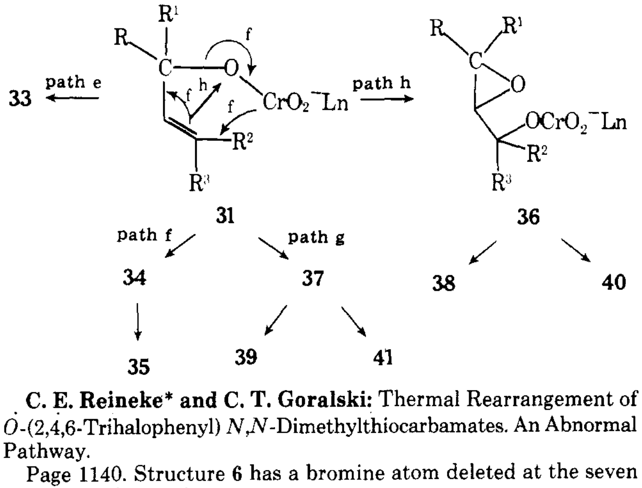
Charles A. Kingsbury,* Dan Draney, Alan Sopchik, William Rissler, and Dana Durham: Survey of Carbon-13–Hydrogen Splittings in Alkenes.

Page 3863. Reference to the elegant earlier work of Vogeli and von Philipsborn, *Org. Magn. Reson.*, **7**, 617 (1975), should have been given.

Vol. 42, 1977

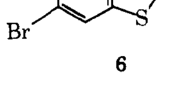
Padmanabhan Sundararaman and Werner Herz*: Oxidative Rearrangements of Tertiary and Some Secondary Allylic Alcohols with Chromium(VI) Reagents. A New Method for 1,3-Functional Group Transposition and Forming Mixed Aldol.

Page 817. The lower part of Scheme II was reproduced incorrectly. The correct formulation is as follows:



C. E. Reineke* and C. T. Goralski: Thermal Rearrangement of *O*-(2,4,6-Trihalophenyl) *N*,*N*-Dimethylthiocarbamates. An Abnormal Pathway.

Page 1140. Structure **6** has a bromine atom deleted at the seven position and should appear as:



6