as seems probable from studies on 1,1-dichloro-3-fluorobutadiene,[19] approximate constants may be deduced as follows: $A = 8.3$, $B = -9.0$, $C = 7.7$.

To the extent that the numerical values of the coefficients in the Karplus equations estimated above can be confirmed and shown to hold in a wider selection of cases, the determination of the ^3J_s coupling constant in butadienoid systems will be useful in determining conformational preferences in butadienes. The *caveat* sounded by Karplus must be continually borne in mind, however.

Acknowledgments. This work was performed with support from the National Science Foundation. We are grateful to Mr. Dennis Wisnosky, to Dr. R. K. Harris, and to Dr. D. F. Koster for technical assistance and for helpful discussions.

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[19] A. A. Bothner-By and D. F. Koster, *J. Am. Chem. Soc.*, **90**, 2351 (1968).

Nuclear Magnetic Resonance Studies of 1,3-Butadienes.[1] V. Conformations of 1,1-Dichloro-3-fluorobutadiene-1,3 and 1,1-Dibromo-3-fluorobutadiene-1,3

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Received October 25, 1967

Abstract: The high-resolution proton magnetic resonance spectra of the title compounds in solution in mixtures of dimethyl ether and dichlorodifluoromethane at temperatures from −130 to +39° have been recorded and analyzed in terms of chemical shifts and coupling constants. The temperature dependence of the $^3J_{HF}$ coupling between the proton on carbon 2 and the fluorine indicates (1) that these compounds exist as mixtures of *s-trans* and skew conformers; (2) that $^3J_{HF}$ in the *s-trans* conformation has the value +25.7 cps (dichloro compound) and +25.2 cps (dibromo compound), while in the skew conformation $^3J_{HF}$ has the value −1.8 cps (dichloro compound) and −1.9 cps (dibromo compound); (3) that for the dichloro compound $\Delta H = 980 \pm 30$ cal, while for the dibromo compound $\Delta H = 1020 \pm 30$ cal, the *s-trans* form being the more stable at low temperatures in each case.

The finding, that the haloprenes exist practically completely in the *s-trans* conformation, while 1,1,3-trichlorobutadiene-1,3 and 1,1,3-tribromobutadiene-1,3 are entirely in a skew form,[2] suggested the investigation of butadienes substituted with groups having intermediate steric requirements. Accordingly 1,1-dichloro-3-fluorobutadiene-1,3 and 1,1-dibromo-3-fluorobutadiene-1,3 have been synthesized, and investigated by means of variable-temperature nuclear magnetic resonance spectroscopy. A secondary reason for choosing these compounds was that the $^3J_{HF}$ coupling constant between the fluorine and the proton on carbon 2 can be observed, and is expected to be dependent on the F-C-C-H dihedral angles.[3-5] It should thus be possible to use it as an indicator of conformer population. Initial experiments[6] over a limited temperature range have confirmed the applicability of the method.

Experimental Section

1,1,1-Trichloro-3-bromo-3-fluorobutane. $CBrCl_3$, 1.5 mol, 0.38 mol of 2-fluoropropene, and 5 g of benzoyl peroxide were heated at 100° for 5 hr in a stainless steel bomb.[7] The bomb was then quickly cooled in ice and the resulting yellowish solution distilled under vacuum. The main product distilled at 87–88° (28 mm), giving an 88.4% yield based on the 2-fluoropropene. The nmr spectrum was consistent with the desired product.

1,1-Dichloro-3-fluoro-1,3-butadiene. 1,1,1-Trichloro-3-bromo-3-fluorobutane (0.15 mol) and 0.30 mol of tri-*n*-butylamine were heated quickly in a flask fitted with a condenser for distillation. At a bath temperature of about 125°, the solution turned yellow. A very sudden reaction occurred at about 145° (bath temperature), turning the reaction mixture black. A small amount of a yellowish liquid was collected in the receiver flask. The distillate was washed with dilute HCl, then water, and dried over $MgSO_4$, then distilled in a Craig apparatus. Product was collected at a bath temperature of 37° (28 mm). The nmr spectrum was consistent with the expected product. The uv spectrum in cyclohexane gave λ_{max} 242 mμ (ϵ 1.8×10^4). Subsequent preparations of the compound gave improved yields if the dehydrohalogenation of the butane was carried out at about 100-mm pressure. This removes the product more quickly from the hot reaction mixture. The most significant impurity, which was evident in the nmr spectrum, was 1,1-dichloro-3-bromo-3-fluoro-1-butene.

1,1,1,3-Tetrabromo-3-fluorobutane. A mixture of 0.22 mol of 2-fluoropropene, 0.75 mol of CBr_4, 5 g of benzoyl peroxide, and 200 ml of cyclohexane was heated at 70° for about 3 hr in a stainless steel bomb.[1] After cooling, the cyclohexane and most of the CBr_4 were distilled off under vacuum. The desired product was con-

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[1] Paper IV of this series: A. A. Bothner-By and E. Moser, *J. Am. Chem. Soc.*, **90**, 2347 (1968).

[2] A. A. Bothner-By and D. Jung, *ibid.*, **90**, 2342 (1968).

[3] J. C. Schug, P. E. McMahon, and H. S. Gutowsky, *J. Chem. Phys.*, **33**, 843 (1960); H. S. Gutowsky, G. G. Belford, and P. E. McMahon, *ibid.*, **36**, 3353 (1962).

[4] M. Takahachi, D. R. Davis, and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 2935 (1962); J. B. Lambert and J. D. Roberts, *ibid.*, **87**, 3891 (1965).

[5] K. L. Williamson, Y.-F. Li, F. H. Hall, and S. Swager, *ibid.*, **88**, 5678 (1966).

[6] A. A. Bothner-By and D. F. Koster in "Magnetic Resonance and Relaxation," R. Blinc, Ed., North-Holland Publishing Corp., Amsterdam, 1967, pp 1054–1056.

[7] M. S. Kharasch, E. V. Jensen, and W. H. Urey, *J. Am. Chem. Soc.*, **69**, 1100 (1947); M. S. Kharasch, O. Reinmuth, and W. H. Urey, *ibid.*, **69**, 1105 (1947).

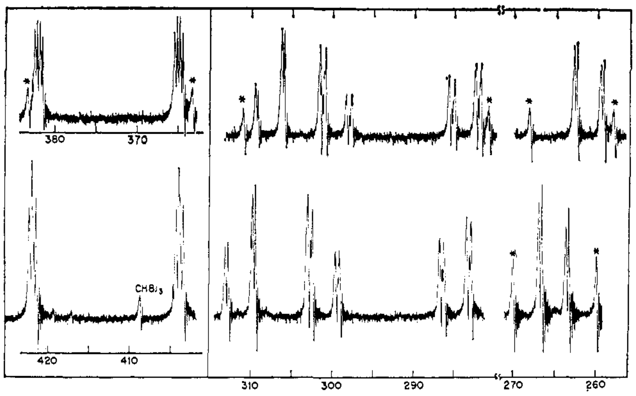


Figure 1. Proton nmr spectra of 1,1-dichloro-3-fluorobutadiene-1,3 (top) and 1,1-dibromo-3-fluorobutadiene-1,3 (bottom) at room temperature in $CFCl_3$ solution. Peak positions are in cycles per second from internal TMS at 60 Mcps; * indicates calibration side band.

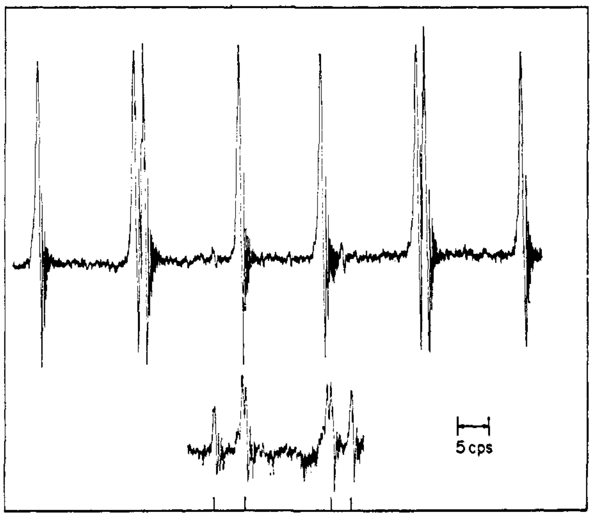


Figure 2. Fluorine nmr spectrum (15 Mcps) of 1,1-dichloro-3-fluorobutadiene-1,3 at room temperature. Bottom trace run at increased radiofrequency power to enhance weak lines.

taminated with CBr_4 and distilled over the range 78–88° (2 mm). The pure product, which distils at 87–88° (2 mm), was obtained by redistillation in 75% yield based on 2-fluoropropene.

1,1-Dibromo-3-fluoro-1,3-butadiene. A solution of 0.013 mol of 1,1,1,3-tetrabromo-3-fluorobutane and 0.03 mol of tri-*n*-butylamine was heated in a flask with a condenser fitted for distillation. The pressure was maintained at about 100 mm. A rapid reaction commenced at 140°, and a small amount of product ($\approx$0.5 cc) was collected. The product was washed with dilute HCl and water and then dried over $MgSO_4$. Small amounts were distilled in a Craig apparatus. The nmr spectrum was consistent with the desired product. The uv spectrum in cyclohexane gave λ_{max} 242 mμ (ϵ 7.92 $\times 10^3$), λ_{max} 218 (ϵ 7.92 $\times 10^3$), and a shoulder at 234 mμ. It was difficult to remove small amounts (<5%) of $CHBr_3$ and 1,1,3-tribromo-3-fluoro-1-butene, which were present as impurities in the nmr spectrum. The mass spectrum showed a 1:2:1 parent peak triplet at *m/e* 228, 230, and 232. An accurate measurement of the 230 peak gave *m/e* 229.8569 (calculated *m/e* 229.8567, $C_4H_3FBr^{79}Br^{81}$).

Sample Preparation. The samples of 1,1-dichloro- and 1,1-dibromo-3-fluorobutadienes were vacuum degassed and sealed in 5-mm precision nmr tubes. The sample concentration was approximately 30% in a 1:1 dimethyl ether-CF_2Cl_2 mixture. Preliminary experiments and analyses were performed on samples at 30% concentration in $CFCl_3$. Mass spectra were obtained on the AEI MS-9.

Spectra. Spectra recorded at temperatures above −60° were run on a Varian A-60 equipped with the V 6040 variable-temperature accessory. Temperature calibration was checked before and after recording each spectrum by measuring methanol peak separations. An average of four spectra (two swept upfield and two downfield) were taken at each temperature. Spectra recorded below −60° were taken on a DP-60 equipped with a variable-temperature probe, and operating at 60 Mcps. The spectrometer was operated in the frequency-sweep mode. Field-frequency lock was provided by an RSI spin decoupler, and the frequency was swept by externally controlling a General Radio Model 1161-A frequency synthesizer. Temperature calibration was checked with a copper-constantan thermocouple. Field-sweep 15.085-Mc proton and fluorine nmr spectra were also recorded on the DP-60, with an auxiliary 15.085-Mcps radiofrequency unit and probe.

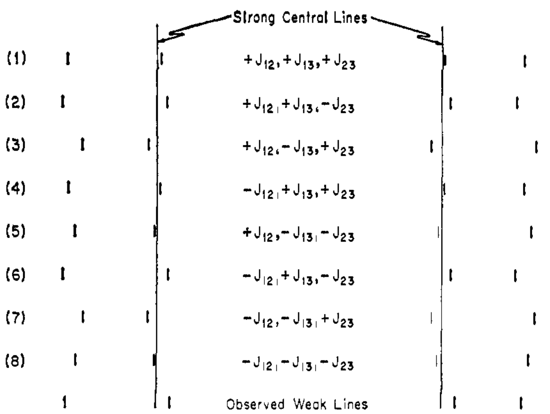
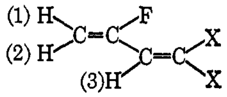


Figure 3. Calculated and observed weak lines in the 15-Mcps fluorine nmr spectrum of 1,1-dichloro-3-fluorobutadiene-1,3.

Results

Analysis of Spectra. The spectra of the two compounds, each at 30% (v/v) concentration in $CFCl_3$, are shown in Figure 1. The temperature of the samples was 37 ± 1°. After first-order analysis was made by eye, least-squares fitting of the spectrum was performed using the LAOCN3 program.[8] The parameters obtained are shown in Table I.

Table I. Nmr Parameters of 1,1-Dichloro-3-fluorobutadiene-1,3 and 1,1-Dibromo-3-fluorobutadiene-1,3 at 37° in 30% (v/v) Solution in $CFCl_3$



	X = Cl	X = Br
ν_1[a]	291.95	294.14
ν_2	281.33	288.37
ν_3	373.56	413.29
J_{12}[b]	−3.18	−3.22
J_{13}	+0.64	+0.54
J_{23}	−0.31	−0.31
J_{1F}	+16.28	+16.08
J_{2F}	+46.45	+46.30
J_{3F}	+17.04	+17.33

[a] Cycles per second downfield from internal tetramethylsilane at 60 Mcps. [b] Cycles per second.

The signs of the H,H and H,F couplings cannot be obtained from the 60-Mcps spectra, which are too nearly first order. However trial calculations indicated that fluorine spectra obtained at 15 Mcps would contain some weak but observable combination lines, whose frequencies would be sensitive to the relative signs of

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(8) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

Table II. $^3J_{HF}$ in 1,1-Dichloro-3-fluorobutadiene and 1,1-Dibromo-3-fluorobutadiene in Dimethyl Ether–CF_2Cl_2 Solutions at Several Temperatures

	$^3J_{HF}$, cps							
	+39°	+10°	−10°	−30°	−52°	−97°	−119°	−130°
$C_4H_3Cl_2F$	17.77	18.47	19.25	19.92	20.85	23.0	23.6	24.0
$C_4H_3Br_2F$	17.75	18.63	19.26	19.88	20.90	22.8	23.5	23.7

the H,H and H,F coupling constants. The fluorine spectrum of 1,1-dichloro-3-fluorobutadiene-1,3 at 15 Mcps is shown in Figure 2 along with a second spectrum obtained using higher radiofrequency power, in order to suppress the more easily saturated first-order lines and to bring out the weaker, nearly forbidden lines.

In view of the positive H,F couplings observed in fluoroprene[9] and 2-fluoropropene[10] it is probable that the H,F couplings are positive. On that assumption, the expected frequencies of the weak lines were calculated for the eight possible sign combinations of the J_{HH}'s. The calculated frequencies together with the observed frequencies are shown graphically in Figure 3. Good agreement is obtained only with sign combinations 2 and 6, *i.e.*, either $J_{12}+$, $J_{13}+$, $J_{23}-$, or $J_{12}-$, $J_{13}+$, $J_{23}-$ (numbering of protons as in Table I). The coupling corresponding to J_{12} in fluoroprene and 2-fluoropropene is negative,[9,10] and the minus sign is accordingly adopted in Table I.

The variation of the $^3J_{HF}$ coupling constants with temperature is shown in Table II, for both compounds. At the lowest temperatures the peaks were broadened, and the values are accordingly given with less precision.

Discussion

It is supposed that two rotational isomers are present in rapid thermal equilibrium at all temperatures reached experimentally, so that the observed nmr parameter J is a population-weighted average

$$J = p_1J_1 + p_2J_2 \qquad (1)$$

where p_1 and p_2 are the fractional populations of forms with coupling constants J_1 and J_2, and $p_1 + p_2 = 1$. An equilibrium constant, K, may then be defined, where

$$K = p_2/p_1 \qquad (2)$$

$$K = \exp(-\Delta H/RT)\exp(\Delta S/R) \qquad (3)$$

From assumed values for ΔH and ΔS, p_2 and p_1 may be computed and the set of eight equations (1) for the eight temperatures solved by least squares for J_1 and J_2. The magnitude of the residuals in the least-square solution gives information about the adequacy of the model and the correctness of the guesses for ΔH and ΔS. It turns out that ΔH and J_1 are reasonably well determined by this process, but that ΔS and J_2 can vary over a sizeable range (but not independently of each other). For the dichloro compound $\Delta H = 980 \pm 30$ cal and $J_1 = 25.7$ cps while for the dibromo compound $\Delta H = 1020 \pm 30$ cal and $J_1 = 25.2$ cps. These values may be compared with $^3J_{HF} = 25.14$ cps in fluoroprene[9] known to be in a planar *s-trans* conformation.[11] The relation between ΔS and J_2 is shown in Figure 4. The least-squares residuals suggest that points on the upper half of the curve are slightly to be preferred to points on the lower half.

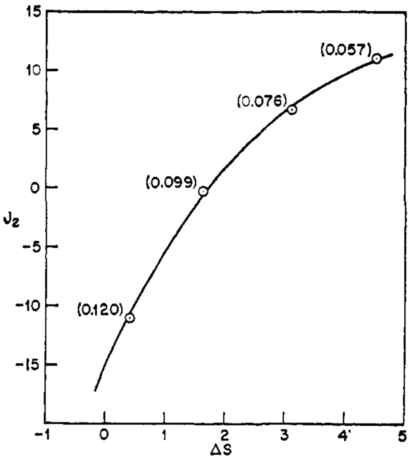

Figure 4. The variation of J_2 with ΔS for 1,1-dichloro-3-fluorobutadiene-1,3. Numbers in parentheses are the residuals squared from the least-square fitting. The curve for the dibromo compound is essentially identical with this one.

It is obvious that both ΔS and J_2 cannot be uniquely determined unless an additional assumption concerning one of them is made. Previous experience,[3-5] as well as studies on a model compound,[12] lead one to expect values in the range 0 to +20 cps for J_2. On the other hand ΔS will be zero if the equilibrium is between an *s-trans* and *s-cis* form or will be $R \ln 2$ if it is between *s-trans* and skew forms (all other contributions to ΔS are assumed identical in the two forms). A zero value for ΔS would give the unrealistic value for J_2 of about −15 cps. For this reason we feel the data are better explained with $\Delta S = R \ln 2$, *i.e.*, that the equilibrium is between one *s-trans* and two skew conformations. J_2 becomes −1.8 and −1.9 cps in the case of the dichloro and dibromo compounds, respectively. It is reasoned that the large 1,4 (H,Cl) repulsion in a *s-cis* arrangement results in a more stable skew isomer.

There are several additional observations which acquire reasonable explanations with the above interpretation.

(1) ΔH for these compounds in CF_2Cl_2–dimethyl ether solution is larger than in $CFCl_3$ solution. The *s-trans* compound is expected to have the largest moment, and should be more stable in a more polar medium.

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(9) A. A. Bothner-By and R. K. Harris, *J. Am. Chem. Soc.*, 87, 3445 (1965).

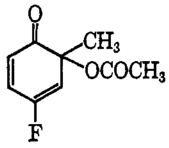
(10) M. Y. DeWolf and J. D. Baldeschwieler, *J. Mol. Spectry.*, 13, 344 (1964).

(11) D. Lide, Jr., *J. Chem. Phys.*, 37, 2074 (1962).

(12) See ref 1.

(2) J_2 is slightly negative for both compounds in CF_2Cl_2–dimethyl ether solution and slightly positive in $CFCl_3$ solution.[6] Again, because of the bond moments, the dihedral angle in the skew form is expected to be smaller (closer to 90°) in the more polar solvent. At 90°, the coupling may well be negative.[5]

(3) The corresponding $^3J_{HF}$ in the model compound 2-methyl-2-acetoxy-4-fluorocyclohexadien-3,5-one (I)



I

is[12] 7.06 cps. This compound is probably nearly planar, and the smaller value of $^3J_{HF}$ in the butadienes indicates a significant twist about the central C–C single bond.

(4) Variable-temperature infrared[13] studies of these butadienes in CS_2 solution indicate the presence of two distinguishable conformers, with $\Delta H = 765$ (dichloro) and 815 (dibromo) cal/mol. This is in excellent agreement with our earlier nmr results in $CFCl_3$ solution.[6]

Acknowledgments. This work was supported by a grant from the National Science Foundation. We are grateful to Mr. D. Wisnosky for technical assistance and Mr. J. R. Boal for recording the mass spectra.

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(13) K. O. Hartman, G. L. Carlson, R. E. Witkowski, and W. G. Fateley, *Spectrochim. Acta*, **24A**, 157 (1968).

Diazenes. I. Decarboxylation of Phenyldiazenecarboxylic Acid

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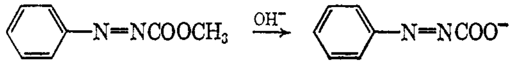
Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790. *Received November 2, 1967*

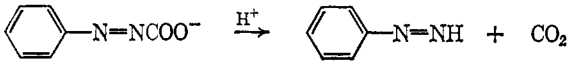
Abstract: The synthesis of several aryldiazenecarboxylic acid[4] esters and their conversion to the corresponding salts, $XArN{=}NCOO^-M^+$, are described. The rate constant for hydrolysis of $C_6H_5N{=}NCOOCH_3$ (**1**) at 4° is $\sim 2.0 \times 10^2$ l. mole^{-1} sec^{-1}, 10^4 faster than that of the homomorphic ester, $C_6H_5CH{=}CHCOOCH_3$. The rate constant for the reaction of **1** with sodium methoxide in anhydrous methanol is $\sim 3 \times 10^{-3}$ l. mole^{-1} sec^{-1} at 25°, and the pK_a of phenyldiazene (**3**), $C_6H_5N{=}NH$, is estimated as no more than 27 from a comparison of the rate constants for reaction with hydroxide ion and methoxide ion. Spectroscopic data (ultraviolet-visible, infrared, and nuclear magnetic resonance) are reported for many of the diazene derivatives. A technique for following the decarboxylation of phenyldiazenecarboxylate anion, $C_6H_5N{=}NCOO^-$ (**2**), in the absence of oxygen has been developed. The rate of decarboxylation varies linearly with hydrogen ion concentration over the pH range 10.4–11.9. Arguments in favor of a mechanism proceeding *via* carbon dioxide loss from the zwitterion $C_6H_5N{=}NH^+COO^-$ are presented.

Aryldiazenecarboxylic (arylazoformic) acids and their derivatives[4] have an old, but rather neglected, place in the chemical literature. The propensity of phenyldiazenecarboxylic acid (**2**) for decarboxylation was discovered by Widman[6] and Thiele.[7] However, the only previous mechanistic study of the process is that of King[8,9] for the rate of nitrogen evolution from diazenedicarboxylic acid ("azodicarboxylic acid"[1]), $HOOCN{=}NCOOH$, over the pH range 11.8–12.8.

Our interest in diazenecarboxylic acid esters (azo esters) was originally aroused by the finding that α-chymotrypsin catalyzed the hydrolysis of methyl phenyldiazenecarboxylate (**1**).[10] We found that an understanding of the decarboxylation process was vital to further work on the hydrolysis rates of **1**. A study of the decarboxylation of **2** is the primary subject of this paper. Discussion of the product of decarboxylation, phenyldiazene (**3**), is too extensive to be included but may be found in the following papers.[5]



1 **2**



2 **3**

Results

The preparation of diazenecarboxylic esters and their properties, the hydrolysis of the ester **1**, the reaction of **1** with methoxide ion in methanol, the isolation of the diazenecarboxylic acid salts, the spectroscopic properties of the diazenecarboxylic acid derivatives, and the decarboxylation of the anion **2** are described in this section.

Esters. Syntheses of the methyl esters of aryldiazenecarboxylic acids of the general formula $XC_6H_4N{=}$

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(1) (a) This work is abstracted in part from the Ph.D. Thesis of P. C. Huang, State University of New York at Stony Brook, Oct 1966; (b) Predoctoral Fellow of the National Institutes of Health, 1964–1966.

(2) Support from the National Science Foundation, the Army Research Office (Durham), and the National Institutes of Health is gratefully acknowledged.

(3) Alfred P. Sloan Fellow, 1960–1964.

(4) See part II of this series[5] for a discussion of nomenclature.

(5) P. C. Huang and E. M. Kosower, *J. Am. Chem. Soc.*, **90**, 2362, 2367 (1968).

(6) O. Widman, *Ber.*, **28**, 1925 (1895).

(7) J. Thiele, *ibid.*, **28**, 2599 (1895).

(8) C. V. King, *J. Am. Chem. Soc.*, **62**, 379 (1940).

(9) C. V. King and J. J. Josephs, *ibid.*, **66**, 767 (1944).

(10) B. M. Goldschmidt, unpublished results.