

m.p. 169–170° dec., purity 100.1% by titration. **N-Bromoacetamide** was prepared by the method of Oliveto and Gerald¹⁶; m.p. 104–107°, purity 99.8%. **N-Chlorosuccinimide** was commercial material rapidly recrystallized from benzene; m.p. 149–150°, purity 98.6%.

Competitive experiments were carried out and products analyzed by gas chromatography essentially as in our NBS work.⁵ Relative reactivities were calculated from direct competitive experiments whenever possible, although a number of

(16) E. P. Oliveto and C. Gerold, *Org. Syn.*, **31**, 17 (1951).

cross checks were carried out as well. The actual competitions carried out are shown in Fig. 1 and 2.¹⁷ Reactions with N-chlorosuccinimide were very slow and required 24 hr. heating at 80° in the presence of benzoyl peroxide for complete reaction. Three experiments yielded relative reactivities for cyclohexane: toluene of 3.0, 3.3, and 5.7, and (using bromobenzene as an internal standard) chlorobenzene was detected among the products.

(17) Direct comparisons for toluene with *o*-xylene, *p*-xylene, and ethylbenzene using hydantoin (I) were carried out by Dr. D. D. Tanner.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

Substitutions at Saturated Carbon-Hydrogen Bonds Utilizing Molecular Bromine or Bromotrichloromethane^{1,2}

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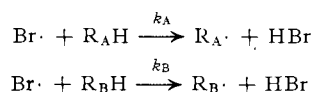
Competitive photobrominations of aralkyl hydrocarbons utilizing molecular bromine or bromotrichloromethane have been performed. The results establish reactivity scales of benzyl-type hydrogen atoms toward the bromine atom and the trichloromethyl radical.

Results

Table I summarizes a number of competitive brominations using molecular bromine in carbon tetrachloride at 40°. The last column of this table lists the relative reactivities calculated by the equation

$$\frac{k_A}{k_B} = \frac{\log ([R_A H]_t / [R_A H]_i)}{\log ([R_B H]_t / [R_B H]_i)}$$

where k_A and k_B are defined as



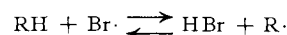
and the subscripts refer to initial and final concentrations.

The data summarized in Table I do not reflect a study of solvent effects in this reaction. The total concentration of aromatic hydrocarbon has been held at about 1 *M* in all of the experiments performed. The consistency of the experiments as summarized in Table II, which summarizes all the experiments of Table I, suggests that solvent effects are not important. It is difficult to estimate the experimental uncertainties involved in the averaged reactivity series given in Table II because of the number of "cross check" experiments. It is felt that the reactivity series has an uncertainty of about $\pm 5\%$.

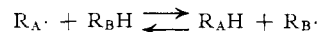
Table III gives data obtained using bromotrichloromethane in carbon tetrachloride solution at 40° as the bromination reagent.⁴ Variation in total aromatic hydrocarbon concentration between 2.5 and 1 *M* did not indicate any solvent effect on the reactivity of the trichloromethyl radical although the reproducibility of duplicate experiments was poor in several cases. Table IV summarizes the experiments of Table III and lists an averaged reactivity scale thought to involve experimental uncertainties not much greater than $\pm 10\%$.

Discussion

Photobrominations utilizing molecular bromine possess the experimental difficulty that the hydrogen abstraction reaction is reversible. In the case of meth-



ane the reaction between the methyl radical and hydrogen bromide occurs more readily than the reaction between methane and the bromine atom.⁵ For the aralkyl hydrocarbons investigated in this study reversal of the hydrogen-abstraction reactions would not be expected to be too important owing to the resonance stabilization of $R\cdot$. Nevertheless high bromine concentrations and a rapid removal of hydrogen bromide were employed to ensure the absence of this complication as well as the absence of exchange reactions of the type



The experimental variations listed in Table I, as well as the agreement between "cross checks" listed in this table, substantiate the assumption that we have measured the relative reactivities of these benzylic carbon-hydrogen bonds without complicating side reactions.

Table V summarizes the effect of structure upon the reactivities of benzylic carbon-hydrogen toward bromine atoms. Available data for the chlorine atom⁶ are given for comparison. Table V was constructed by combining the data for liquid phase competitive brominations of benzylic hydrogen atoms with vapor phase data for alkanes.⁷ The data used for alkanes (per hydrogen atom) were: methane, $\log PZ = 13.4$, $E_a = 18.3$; ethane, $\log PZ = 13.11$, $E_a = 13.4$; propane (2° H), $\log PZ = 13.41$, $E_a = 10.15$; isobutane (3° H), $\log PZ = 13.3$, $E_a = 7.5$.⁸ The 3°-hydrogen atoms of isobutane and 2,3-dimethylbutane have been assumed to have equal reactivity toward the bromine atom in order that the benzylic hydrogen atoms and the alkanes could be compared.⁹

As far as the bromine atom is concerned, Table V gives a very consistent picture. Comparisons in a horizontal direction from left to right represent acti-

(5) H. C. Andersen and G. B. Kistiakowsky, *J. Chem. Phys.*, **11**, 6 (1943); G. B. Kistiakowsky and E. R. Van Artsdalen, *ibid.*, **12**, 469 (1944).

(6) G. A. Russell, A. Ito, and D. G. Hendry, *J. Am. Chem. Soc.*, **84**, 2976 (1963).

(7) G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 4177 (1960).

(8) *PZ* in cc. mole⁻¹ sec.⁻¹; E_a in kcal. mole⁻¹.

(9) Rate data for the vapor phase photobromination of toluene (H. R. Anderson, H. A. Scheraga, and E. R. Van Artsdalen, *J. Chem. Phys.*, **21**, 1258 (1953)), $E_a = 7.2 \log PZ$ (per α -hydrogen atom) = 13.05, would give a relative reactivity for toluene of 17,000. However, these data have been criticized (S. W. Benson and J. H. Buss, *ibid.*, **28**, 301 (1958)).

(1) Directive Effects in Aliphatic Substitutions. XVIII.

(2) This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the donors of this fund.

(3) (a) Alfred P. Sloan Foundation Fellow, 1959–1963; (b) National Science Foundation Undergraduate Research Participant, 1960–1962.

(4) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 391, 394 (1960).

TABLE I
 PHOTOBROMINATION IN CARBON TETRACHLORIDE SOLUTION AT 40°

Hydrocarbon A	Hydrocarbon B	[A] ₁ ^a	[A] ₁ ^a	[B] ₁ ^a	[B] ₁ ^a	Rate of liq. Br ₂ addn., cc. per min.	Rate of nitrogen sweep, cc. per min.	k _A /k _B
Cumene	Ethylbenzene	0.439	0.250	0.517	0.294	0.2	30	1.00
Cumene	Ethylbenzene	.442	.246	.511	.292	.2	100	1.05
Cumene	Ethylbenzene	.451	.255	.514	.306	60	100	1.10
Cumene	Ethylbenzene	.443	.157	.517	.210	0.2	100	1.14
Cumene	Diphenylmethane	.484	.264	.492	.357	.2	100	1.87
Cumene	Diphenylmethane	.485	.256	.480	.331	.2	30	1.73
Cumene	Diphenylmethane	.234	.070	.495	.275	.2	100	2.07
Cumene	Diphenylmethane	.486	.184	.246	.150	.2	100	1.95
Cumene	Diphenylmethane	.320	.175	.290	.200	.1	100	1.64
Cumene	Triphenylmethane	.789	.534	.660	.528	.2	100	1.77
Cumene	Triphenylmethane	.530	.326	.580	.515	.3	100	4.12
Cumene	1,1-Diphenylethane	.747	.564	.723	.493	.2	100	0.74
Cumene	1,1-Diphenylethane	.482	.174	.485	.306	.2	100	0.83
Cumene	Dibenzyl	.809	.375	.723	.627	.2	100	5.32
Ethylbenzene	Toluene	.570	.177	.339	.306	.1	100	11.6
Ethylbenzene	Diphenylmethane	.744	.483	.937	.717	.2	100	1.6
Ethylbenzene	Triphenylmethane	.476	.184	.592	.376	.1	100	2.12
Ethylbenzene	1,1-Diphenylethane	.500	.380	.532	.372	.12	100	0.80
Toluene	Diphenylmethane	.445	.312	.588	.524	.1	100	.15
Toluene	Triphenylmethane	.424	.382	.592	.381	.1	100	.18
Toluene	2,3-Dimethylbutane	.472	.328	.472	.432	.2	30	4.13
Toluene	2,3-Dimethylbutane	.476	.322	.460	.429	.2	30	5.70
Triphenylmethane	Diphenylmethane	.292	.186	.305	.174	.2	100	0.81
Triphenylmethane	1,1-Diphenylethane	.596	.336	.508	.160	.1	100	0.50

^a Moles per liter.
 TABLE II
 RELATIVE REACTIVITIES TOWARD BROMINE ATOMS AT 40°

	Competitive reacn. with cumene	Competitive reacn. with ethylbenzene	Competitive reacn. with diphenylmethane	Competitive reacn. with triphenylmethane	Av. rel. reactivity	Reactivity per hydrogen atom
Toluene	..	0.080	0.080	0.087	0.082	1.00 ^a
Ethylbenzene	0.93	0.093 ^a	0.93	17.2
Cumene	1.00 ^a	1.00 ^a	37.0
Diphenylmethane	0.54	0.52	0.53 ^a	..	0.53	9.6
Triphenylmethane	0.58	0.44	0.43	0.48 ^a	0.48	17.8
1,1-Diphenylethane	1.26	1.16	..	0.96	1.13	42.0
Bibenzyl	0.18	0.18	1.7
2,3-Dimethylbutane	0.017 ^c	0.3 ^b

^a Assumed. ^b Per 3°-hydrogen atom. ^c From Table I.
 TABLE III
 COMPETITIVE BROMINATION WITH BROMOTRICHLOROMETHANE IN METHYLENE CHLORIDE AT 40°

Hydrocarbon A	Hydrocarbon B	[A] ₁ ^a	[A] ₁ ^a	[B] ₁ ^a	[B] ₁ ^a	k _A /k _B
Ethylbenzene	Toluene	0.648	0.208	1.864	1.692	36
Ethylbenzene	Toluene	.656	.100	1.880	1.460	23
Ethylbenzene	Cumene	.488	.414	0.489	0.271	0.28
Ethylbenzene	Cumene	.594	.516	.514	.304	.27
Ethylbenzene	Cumene	.481	.218	.429	.035	.39
Ethylbenzene	Cumene	.852	.348	.290	.050	.50
Ethylbenzene	Cumene	1.470	1.225	1.075	.730	.48
Ethylbenzene	Cumene	1.524	0.185	1.075	.052	.59
Ethylbenzene	Diphenylmethane	0.257	.215	0.277	.222	.81
Ethylbenzene	Diphenylmethane	.532	.430	.448	.372	1.1
Cumene	Triphenylmethane	.530	.440	.580	.481	0.99
Cumene	Triphenylmethane	.530	.337	.580	.366	.98
Cumene	1,1-Diphenylethane	.964	.732	.970	.514	.43
Cumene	1,1-Diphenylethane	.964	.730	.971	.454	.36
Diphenylmethane	Triphenylmethane	.305	.130	.220	.164	1.5

^a Moles per liter.

vation of a given hydrogen atom by substitution of a methyl group for an α -hydrogen atom. In all cases a second or third substitution fails to produce as large an effect as the first methyl substitution. Further-

more, the activation produced by methyl substitution decreases as reactivity of the hydrocarbon is increased by phenyl substitution. Thus, conversion of toluene to ethylbenzene increases the reactivity of the α -

TABLE IV
RELATIVE REACTIVITIES TOWARD THE TRICHLOROMETHYL RADICAL AT 40°

Hydrocarbon	Com- peti- tive reacn. with ethyl- ben- zene	Com- peti- tive reacn. with cumene	Com- peti- tive reacn. with phenyl- methane	Av. rel. reactivity	Rel. reactivity per α - hydrogen atom
Toluene	0.03	0.03	1.00 ^a
Ethylbenzene	1.0 ^a	1.0 ^a	50
Cumene	2.6	2.6 ^a	...	2.6	260
Diphenylmethane	0.95	...	0.95 ^a	0.95	50
Triphenylmethane	...	2.6	0.64	1.6	160
1,1-Diphenylethane	...	6.5	...	6.5	650

^a Assumed.

TABLE V
EFFECT OF STRUCTURE ON RELATIVE REACTIVITIES OF BENZYLIC HYDROGEN ATOMS

	CH ₃ H	CH ₃ CH ₂ -H	(CH ₃) ₂ CH-H	(CH ₃) ₃ C-H
Br	0.0007	1.00 ^a	220	19,400
Cl	0.004	1.00 ^a	4.3	6.0

	C ₆ H ₅ CH ₂ -H	C ₆ H ₅ CH(CH ₃)-H	C ₆ H ₅ C(CH ₃) ₂ -H
Br	64,000	1,000,000	2,330,000
Cl	1.3	3.3	7.3
CCl ₃	1.00	50	260

	(C ₆ H ₅) ₂ CH-H	(C ₆ H ₅) ₂ C(CH ₃)-H
Br	620,000	2,700,000
Cl	2.6	...
CCl ₃	50	650

	(C ₆ H ₅) ₃ C-H
Br	1,140,000
Cl	9.5
CCl ₃	160

^a Assumed.

hydrogen atom by 15-fold, whereas 1,1-diphenylethane is only 4.4 times as reactive as diphenylmethane.

Comparison of the vertical columns of Table V gives a consistent picture of activation produced by substitution of phenyl for hydrogen. Again, a saturation effect is found in that the activation decreases as the number of phenyl substitutions increase.

Comparison of reactivities in a diagonal direction presents a consistent picture of the effect upon reactivity of replacing a methyl group by a phenyl group. Such substitution produces an activating effect which decreases as the activity of the alkane increases. Thus, a benzylic hydrogen atom of toluene is 64,000 times as reactive as a hydrogen atom of ethane, whereas the benzylic hydrogen atom of cumene is only 130 times as reactive as the 3°-hydrogen atom of isobutane. Further substitution of phenyl for methyl groups gives rise to little activation or to actual deactivation. This is probably due to different polar effects of methyl and phenyl substituents. Replacement of a hydrogen atom in an alkane by either phenyl or methyl will increase the reactivity of the remaining α -hydrogen atoms toward the bromine atom by virtue of the increased stability of the resulting alkyl radical with phenyl having a greater resonance-stabilizing effect than methyl. However, as the reactivity of a hydrogen atom becomes high, a further increase in resonance stabilization of the resulting alkyl radical is apparently not as important as a change in the electron density of the bond. Thus, the α -hydrogen atoms of 1,1-diphenylethane are over twice as reactive as the benzylic

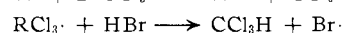
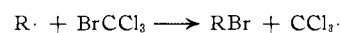
hydrogen atom in triphenylmethane. Such effects are more important in the reactions of the more reactive chlorine atom. Thus, there is a gradual decrease in reactivity of a 2°-hydrogen atom as methyl groups are replaced in propane (4.3) to give ethylbenzene (3.3) and diphenylmethane (1.3). This decrease in reactivity upon substitution of a phenyl for an alkyl group, if due to a polar effect, should occur only when the attacking atom or radical has a high electron affinity. This appears to be the case since (Table VI) toward phenyl or polystyrenyl radicals diphenylmethane is considerably more reactive than ethylbenzene and triphenylmethane more reactive than cumene. There is little evidence for this effect in the reactivity series given for *t*-butoxy radicals or peroxy radicals in Table VI although we might have expected this effect to occur for these radicals owing to their high electron affinity.

TABLE VI
REACTIVITIES OF ARAKYL HYDROCARBONS TOWARD FREE RADICALS

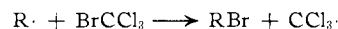
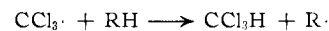
Hydrocarbon	Relative reactivity ^a			
	Phenyl ^b (60°)	Polystyrenyl ^c (60°)	<i>t</i> -Butoxy ^d (40°)	Peroxy ^e (90°)
Toluene	1.00 ^f	1.00 ^f	1.00 ^f	1.00 ^f
Ethylbenzene	4.4	8.2	3.2	7.8
Diphenylethane	7.5	28	4.7	16
Cumene	9.7	20	6.8	13
Triphenylmethane	39	85	9.6	13

^a Per α -hydrogen atom. ^b Unpublished work with Dr. Robert F. Bridger. ^c R. A. Gregg and F. R. Mayo, *Discussions Faraday Soc.*, **2**, 328 (1947). ^d C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108, 6113 (1960). ^e G. A. Russell, *ibid.*, **78**, 1047 (1956). ^f Assumed.

The data of Table V indicate a considerably greater selectivity in bromination with bromotrichloromethane than with molecular bromine. However, the same reactivity trends are observed as for bromination with molecular bromine. This eliminates as a possible mechanism a bromination sequence involving a three-step propagation.



The only alternative appears to be hydrogen abstraction by the trichloromethyl radical as suggested by Huyser.⁴



The reactivity data of benzylic hydrogen atoms toward trichloromethyl reported herein are considerably different from that reported previously by Kooyman.¹⁰ Kooyman's reactivity series is based on the ability of aralkyl hydrocarbons to reduce the yield of 1-hexadecene-carbon tetrachloride addition products in a benzoyl peroxide-catalyzed telomerization. Although the process can be justified kinetically, its interpretation is by no means straightforward.¹¹ The present results suggest (see Table VII) that the reactivities measured by the retardation of telomerization are connected with some other intermediate(s) than the trichloromethyl radical.

Experimental

Reagents.—All reagents were commercial materials which were distilled or recrystallized before use. Gas-liquid chromatograph (g.l.c.) showed all materials to be 99 mole % pure or

(10) E. C. Kooyman, *Discussions Faraday Soc.*, **10**, 163 (1951); E. C. Kooyman and E. Farenhorst, *Trans. Faraday Soc.*, **49**, 58 (1953).

(11) G. A. Russell, "Technique of Organic Chemistry," Vol. 8, Part I, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1961, p. 343.

TABLE VII
RELATIVE REACTIVITIES OF ARALKYL HYDROCARBONS TOWARD
THE TRICHLOROMETHYL RADICAL^a

Hydrocarbon	CCl ₄ , 40° (this work)	From retardation of telomerization, 91.5° (ref. 10)
Toluene	1.00 ^b	1.00 ^b
Ethylbenzene	50	3.1
Cumene	260	4.2
Diphenylmethane	50	8.0
Triphenylmethane	160	16.7

^a Per α -hydrogen atom. ^b Assumed.

better except for bromotrchloromethane (Eastman practical grade) which was about 96 mole per cent pure. All reagents except for bromotrchloromethane and elemental bromine were dried by percolation through activated silica gel before use.

Procedure for Reactions with Elemental Bromine.—Approximately 25 mmoles of each of two hydrocarbons and 15 mmoles of bromobenzene were accurately weighed out and diluted to 50 ml. with carbon tetrachloride. This was the reaction mixture. Since the bromobenzene did not react under the bromination conditions it was used as the internal standard for the g.l.c. analysis. Experiments in which the internal standard was added after bromination gave the same results as those in which the bromobenzene was present during reaction. The reaction mixture was placed in a 100-ml. three-necked round-bottomed Pyrex flask equipped with a nitrogen inlet tube to remove hydrogen bromide from the solution, a cold finger condenser containing Dry Ice and carbon tetrachloride, a dropping funnel for bromine, and a magnetic stirrer. The flask was immersed in a $40 \pm 0.5^\circ$ water bath and illuminated with a 100-watt unfrosted tungsten

lamp. Enough bromine was added dropwise to react with approximately half of the hydrocarbons present. The rates of addition of bromine and nitrogen were varied in several reactions. After the reaction was completed, the reaction mixture was hydrolyzed to remove lachrymatory products and analyzed by g.l.c. In competitive brominations involving toluene no products of ring substitution could be detected by g.l.c. indicating that less than 1% of the toluene reacting in these reactions was converted to products of nuclear substitution.

Procedure with Bromotrchloromethane.—Approximately 25 mmoles of each of two hydrocarbons and 15 mmoles of bromobenzene were accurately weighed and diluted with carbon tetrachloride. About 5 ml. of the reaction mixture and an equal volume of bromotrchloromethane were placed in a Pyrex ampoule, degassed by freeze-thawings, and sealed. The tube was immersed in a $40 \pm 0.5^\circ$ water bath and illuminated with a 275-watt sun lamp. Under these conditions about half of the hydrocarbons was consumed in 24 hr. The tubes were opened and the contents analyzed by g.l.c. soon after the reaction was quenched.

The choice of column and gas chromatograph was dictated by the hydrocarbon mixture being analyzed. For mixtures which had widely separated boiling points, an F. and M. model 500 gas chromatograph was used and the temperature was hand programmed during the analysis. Another procedure for mixtures with widely separated boiling points was to add two internal standards and make two separate analyses at uniform temperatures. For analyses wherein no temperature change was required during the analysis a Perkin-Elmer Model 154D vapor fractometer with thermistor detector was used. The columns used, either separately or in series, were a 2-m. diisodecyl phthalate, a 1-m. methyl silicone grease, a 1-m. Apiezon N, a 2-m. *n*-propyl tetrachlorophthalate, a 1-m. β,β' -oxydipropionitrile, and a 1-m. column of silicon grease (G. E. XF1105) column in which 5% of the methyl groups have been replaced by cyano-methyl groups.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

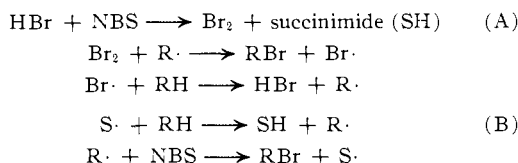
Directive Effects in Aliphatic Substitutions. XIX. Photobromination with N-Bromosuccinimide¹

BY GLEN A. RUSSELL² AND KATHLEEN M. DESMOND

RECEIVED MARCH 27, 1963

Competitive photobromination of aralkyl hydrocarbon in methylene chloride solution at 40° by N-bromosuccinimide yields a relative reactivity series so similar to that observed in photobromination by molecular bromine that it appears that under the reaction conditions both reactions involve the bromine atom as the hydrogen abstracting species.

There is considerable evidence that photobromination by N-bromosuccinimide (NBS) proceeds through a free alkenyl or aralkyl radical. For example, the occurrence of allylic rearrangement³ and the essentially complete racemization observed in the bromination of (—)-ethylbenzene- α -*d*⁴ are consistent with such a radical mechanism. However, the question as to whether the free radical is formed by process A or B or by both A and B has never been completely resolved.



Competitive brominations of substituted toluenes has been interpreted as evidence in support of process B⁵ and process A.⁶ *cis-trans* Isomerization of unreacted olefins has also been interpreted in terms of mechanism

B⁴ as well as process A.⁷ The formation of dibromides in NBS reactions with certain olefins⁸ would seem to support process A or a competing ionic process whereas the formation of 1:1 adducts between NBS and other olefins⁹ can be interpreted in terms of process B.

Another complication rests in the fact that as usually performed the Wohl-Ziegler reaction utilizes refluxing carbon tetrachloride as a solvent. Both NBS and succinimide are rather insoluble in carbon tetrachloride and a third possible reaction mechanism involving succinimidyl radical propagation occurring on the surface of NBS crystals has been suggested.¹⁰ To avoid this problem we have studied the competitive bromination of a series of aralkyl hydrocarbons in methylene chloride solution at 40° , a solvent in which NBS is soluble to the extent of *ca.* 0.25 M.

Results

The competitive photochemical bromination of toluene and ethylbenzene by NBS in refluxing methylene chloride solution was carefully studied as a function of hydrocarbon and NBS concentrations. Sufficient NBS was employed so that upon completion of

(1) This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this Fund.

(2) Alfred P. Sloan Foundation Fellow 1959–1963.

(3) G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944).

(4) H. J. Dauben, Jr., and L. L. McCoy, *J. Am. Chem. Soc.*, **81**, 5404 (1959).

(5) E. C. Kooyman, R. van Helden, and A. F. Bickel, *Koninkl. Ned. Akad. Wetenschap., Proc.*, **66B**, 75 (1953).

(6) F. L. J. Sixma and R. H. Riem, *ibid.*, **61B**, 183 (1958).

(7) B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc.*, 80 (1961).

(8) P. L. Southwick, L. A. Pursglove, and P. Numerof, *J. Am. Chem. Soc.*, **72**, 1600 (1950); E. J. Corey, *ibid.*, **75**, 2251 (1953).

(9) P. Couvreur and A. Bruylants, *Bull. soc. chim. Belges*, **61**, 253 (1952); W. J. Bailey and J. Bello, *J. Org. Chem.*, **20**, 525 (1955).

(10) L. Horner and E. H. Winkelmann, *Angew. Chem.*, **71**, 349 (1959).