TABLE V

PROPERTIES AND ANALYSES OF SUBSTITUTED NEOPHYL p-BROMOBENZENESULFONATES

Substituent	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
p-Br	116–117	$C_{16}H_{16}O_3SBr_2$	42.87	43.05	3.60	3.87
p-COOCH$_3$	117–118	$C_{18}H_{19}O_5SBr$	50.59	50.70	4.48	4.59
p-(C$_6$H$_5$)$_2$CH	112 dec.	$C_{29}H_{27}O_3SBr$	65.04	65.17	5.08	5.07
p-CH$_3$	91–92 dec.	$C_{17}H_{19}O_3SBr$	53.27	53.29	5.00	5.18
m-CH$_3$	89–90[a]	$C_{17}H_{19}O_3SBr$	53.27	53.15	5.00	4.89

[a] Mixed m.p. with p-isomer, 74–90°.

cooled and poured into water. The products were extracted with 5 portions of pentane, and the extracts were washed with water and aqueous sodium bicarbonate. The extract was dried and the solvent was distilled off carefully through a Vigreux column. The crude products were reduced with 1.5 g. of lithium aluminum hydride in ether. The products were isolated by adding water to the solution and decanting the ether solution from the insoluble salts. The solids were extracted several times with ether and the extracts were washed with water, dried and concentrated. Chromatography on 200 g. of alumina separated the products into olefin and alcohol. The olefins, 3.2 g. (59.6%), n^{25}D 1.5207, were eluted with pentane and the alcohols, 1.90 g. (31.1%), n^{25}D 1.5128, b.p. 65–68° (1.5 mm.), were eluted with ether.

The olefin fraction in isoöctane displayed an ϵ 6912 at λ 244 mμ in ultraviolet absorption. A 0.8843-g. sample of the olefin product was hydrogenated in acetic acid at 27.5° and 752 mm., using 10% palladium-on-charcoal as catalyst. A total of 169 cc. of hydrogen (99%) was absorbed in 90 minutes. The hydrogenated product was isolated by pouring the acetic acid solution into water and extracting with pentane. The pentane extracts were washed with aqueous sodium bicarbonate and dried. The solvent was evaporated, and the residue was refluxed with sodium metal until the metal remained bright. A final distillation gave 0.45 g. of product, b.p. 172°, n^{25}D 1.4837. The infrared spectrum of this material was identical with that of isobutylbenzene,[6] n^{25}D 1.4841.

The alcohol fraction from the chromatography of the solvolysis product had m.p. 25–26°, mixed m.p. with 1,1-dimethyl-2-phenylethanol, 25–26°. The infrared spectrum indicated the presence of 0.5–0.75% of neophyl alcohol in the tertiary alcohol. Definite absorption was observed at 1000–1075 cm.$^{-1}$ where neophyl alcohol absorbs strongly, and slightly low absorption was observed at 1125–1150 cm.$^{-1}$ where neophyl alcohol is relatively transparent. The infrared spectrum of the solvolysis product was intermediate between a synthetic mixture containing 1.6% neophyl alcohol in the tertiary alcohol and the pure tertiary alcohol.

In a second solvolysis carried out as above with slightly less pure p-bromobenzenesulfonate, a 61.5% yield of olefin was obtained and a 30.3% yield of alcohol. The olefin fraction, n^{25}D 1.5200, displayed ϵ 6880 at λ 244 mμ in ultraviolet absorption. The alcohol, m.p. and mixed m.p. 24.5–25.5°, b.p. 65–68° (2 mm.), n^{25}D 1.5120, had an infrared spectrum consistent with the presence of more than 99% tertiary alcohol and ca. 1% neophyl alcohol.

In a control experiment, a solution of 1.5 g. of the tertiary alcohol, 1 cc. of acetic anhydride, 1 cc. of 1.00 M lithium acetate in dry acetic acid and 100 cc. of dry acetic acid was heated to 75.0° for 30 hr. The reaction mixture was worked up in the usual way, and the recovered product was reduced with 0.5 g. of lithium aluminum hydride in ether. The excess hydride decomposed with water, and the ether solution was decanted from the salts. The salts were extracted several times with fresh ether. The combined extracts were washed with water, dried and concentrated. Distillation gave 1.3 g. of product, b.p. 65° (1.5 mm.), n^{25}D 1.5130, m.p. 24–25.5°. A comparison of the –OH band at 3350 cm.$^{-1}$ of the product with that of pure tertiary alcohol showed the product to contain a small amount of non-hydroxylic material, probably olefin. Otherwise, the infrared spectra of the two materials were very similar.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Mechanisms of Elimination Reactions. XVIII. Reactivities of Some 2,3-Norbornane Derivatives[1,2]

BY STANLEY J. CRISTOL AND ERHARD F. HOEGGER

RECEIVED JANUARY 18, 1957

Rate constants have been determined for the second-order reaction of sodium 1-pentoxide in 1-pentanol with *endo-cis-* and *trans*-2,3-dichloronorbornane at 101.3 and 116.2°, and with *exo*-2-p-toluenesulfonyl-*endo*-3-chloronorbornane at 0 and at 12°. The relative reactivities toward elimination of the elements of hydrogen chloride from these boat-form cyclohexane rings have been interpreted on the basis of an elimination process involving a carbanion intermediate.

Elimination of the elements of hydrogen chloride from 11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene with alkali has been shown[3] to be very sluggish and to be relatively non-stereospecific, *cis* elimination being preferred over *trans* by a factor of about 8, in contrast to the generally observed large preference of *trans* over *cis* elimination.[4] The striking lack of stereospecificity was rationalized[3] by the assumption that normal *trans* elimination (in acyclic systems or in cyclic systems without severe hindrance to rotation or ring conversion) utilizes a concerted *trans* coplanar transition state[4,5]; this transition state is forbidden to *cis* groups in ordinary small rings or to either *cis* or *trans* groups in bicyclo[2,2,2]octane derivatives without excessive torsional strain. Norbornane, or bicyclo[2,2,1]-heptane is locked by the 1,4-methano bridge in a boat-form cyclohexane ring in the same way as the 1,4-ethano bridge affects the cyclohexane ring in

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[1] Previous paper in series: S. J. Cristol, F. R. Stermitz and P. S. Ramey, THIS JOURNAL, **78**, 4939 (1956).

[2] This work was reported at the 14th National Organic Chemistry Symposium at Lafayette, Indiana, June 13, 1955.

[3] S. J. Cristol and N. L. Hause, THIS JOURNAL, **74**, 2193 (1952).

[4] See, for example: (a) S. J. Cristol, *ibid.*, **69**, 338 (1947); (b) S. J. Cristol, N. L. Hause and J. S. Meek, *ibid.*, **73**, 674 (1951); (c) S. J. Cristol and W. P. Norris, *ibid.*, **76**, 3005 (1954).

[5] D. H. R. Barton and E. Miller, *ibid.*, **72**, 1066 (1950).

TABLE I

DATA, REACTION RATE CONSTANTS AND QUANTITIES OF ACTIVATION FOR DEHYDROCHLORINATION WITH SODIUM 1-PENTOXIDE IN 1-PENTANOL

Compound	Temp., °C.	(Halide) *M*	(Base) *M*	k, l./sec./mole	$k_{110°}$	$E_{act.}$, kcal./mole
endo-cis-2,3-Dichloronorbornane	116.2	0.022	0.42	4.9×10^{-6}	2×10^{-6}[a]	31
		.022	.31	5.0×10^{-6}		
			Av.	5.0×10^{-6}		
	101.3	.034	.19	1.05×10^{-6}		
		.034	.37	9.7×10^{-7}		
			Av.	1.01×10^{-6}		
trans-2,3-Dichloronorbornane[c]	116.2	0.011	.07	3.2×10^{-4}	1.7×10^{-4}[a]	32
		.034	.19	3.6×10^{-4}		
		.024	.14	3.3×10^{-4}		
			Av.	3.4×10^{-4}		
	101.2	.022	.23	6.7×10^{-5}		
		.022	.12	6.5×10^{-5}		
			Av.	6.6×10^{-5}		
exo-2-*p*-Toluenesulfonyl-*endo*-3-chloronorbornane	11.96	.0074	.0094	2.27×10^{-2}	1.2×10^{2}[b]	19
		.0075	.0141	2.05×10^{-2}		
			Av.	2.16×10^{-2}		
	0.00	.0075	.0236	4.85×10^{-3}		
		.015	.0236	4.97×10^{-3}		
			Av.	4.91×10^{-3}		

[a] Interpolated. [b] Extrapolated. [c] The initial halide concentrations recorded were corrected as described in the Experimental section.

the bicyclo[2,2,2]octane molecule. Accordingly, it would be anticipated that 2,3-dichloronorbornane isomers would be relatively inert and that *trans* elimination would not be markedly faster, and might be slower, than *cis* elimination. That this was true was observed in either a qualitative or a rough quantitative fashion in such compounds in three different laboratories.[6-8] In view of these results, it seemed worthwhile to get quantitative information about these isomers.

The preparations of *endo-cis*-2,3-dichloronorbornane and the *trans* isomer has been described,[7,8] and treatment with alkali has been shown to give 2-chloronorbornene.[7] We chose to use 1-pentanol as solvent for the kinetic study, and sodium 1-pentoxide as base, because of the moderately high temperatures involved. Appropriate details of the procedures used in determining rate constants are given in the Experimental section. The rate data are given in Table I for the reactions of these two isomers with sodium 1-pentoxide.

It may be noted from the data of the table that just as in the case of the dichlorodihydroethanoanthracenes, *cis*-dehydrochlorination is preferred over *trans*-dehydrochlorination in these rigid boat-form compounds where the eclipsed bonds cannot readily attain the requisite geometry for *trans* coplanar elimination. These data are not directly comparable with the data on the bicyclooctanes because of the different solvents used (ethanolic dioxane and *n*-amyl alcohol), but it may be fairly stated that in both cases, the favoring of *cis* elimination does not follow from factors increasing its rate, but rather from factors markedly decreasing the rate of *trans* elimination.[3] At the present time we are not in a position to discuss the preference of *cis* elimination over *trans* in the two systems, nor the differences in amount of this preference between the two systems. These may be the result of effects of solvent size and steric hindrance to solvation in the transition state of the various carbanions being formed, but discussion of speculations of this sort must await the accumulation of further data. It would also be desirable to have data on the *exo-cis*-dichloride, but this compound has not yet been described in the literature.

Two alternative processes have been suggested for bimolecular elimination in systems where the groups being eliminated cannot easily attain a *trans*-coplanar conformation. One suggestion has been made that the additional energy of activation required for the less favored process is used partly to twist the molecule more nearly into the requisite geometry and partly to force the mechanism against the still imperfect geometry,[9] but that the process is still concerted, removal of the proton by base being accompanied by formation of the multiple bond and loss of the anion. Unfortunately it seems difficult to define an experimental test for this postulate.

On the other hand, it has been suggested[4a] that a distinctly different mechanism is utilized by those compounds with geometry unfavorable to a *trans* coplanar transition state. This mechanism involves a first step in which the β-proton is transferred to the base to give a carbanion intermediate. The carbanion ultimately loses an anion to form the olefinic or acetylenic product. Energy calculations appear consistent with observed activation energies.[4b] The small amount of deuterium exchange observed in elimination with β-benzene hexachloride (*cis* elimination) was suggested as offering sup-

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[6] H. Bluestone, R. E. Lidov and S. B. Soloway, private communication.

[7] J. D. Roberts, F. O. Johnson and R. A. Carboni, THIS JOURNAL, **76**, 5692 (1954).

[8] N. L. Hause, Ph.D. dissertation, University of Colorado, 1950.

[9] E. D. Hughes, C. K. Ingold and R. Pasternak, *J. Chem. Soc.*, 3832 (1953).

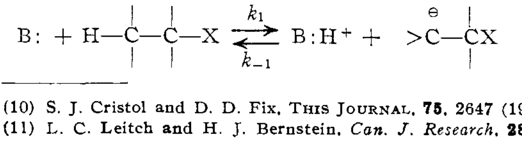
port to the postulated carbanion process.[10] Substantial amounts of deuterium exchange have been observed in treatment of trichloroethylene with alkali,[11] a fact consistent with a carbanion intermediate in elimination where the tendency to abstract a proton from solvent competes favorably with loss of chloride ion.

Another deduction from the dual mechanism theory is that substitution of electron-attracting substituents on the β-carbon atom would minimize the difference in reactivity and energy of activation between the two processes, as it appeared that the carbanion process (where a large negative charge was being developed on the β carbon atom in the transition state) would be more sensitive to the effect of such groups than the concerted process (where the negative charge was being distributed more widely). Such an effect has been observed.[4c,12]

Such an electron-attracting group is a sulfone group, and it might be anticipated that such a group would stabilize the carbanion process markedly. This group (or any other electron-attracting group) might, for example, result in a situation where a stabilized carbanion process might be favored over an alternative concerted elimination process where no activation is present. Indeed, Bordwell and Kern[13] have shown that a *cis* hydrogen activated by the presence of a sulfone group on the same carbon atom will be removed in preference to a *trans* unactivated hydrogen in *trans*-2-*p*-toluenesulfonylcyclohexyl *p*-toluenesulfonate and the corresponding cyclopentyl compounds. In addition, Weinstock, Pearson and Bordwell[14] have shown that the sulfone group has a powerful activating influence in both *cis* and *trans* elimination, although they have not interpreted their data in terms of possible carbanion mechanisms.[15]

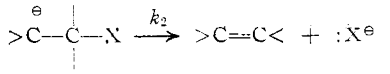
We were interested in how the sulfone group might affect elimination rates in boat-form cyclohexane rings and accordingly data were obtained on *exo*-2-*p*-toluenesulfonyl-*endo*-3-chloronorbornane,[16] and they are recorded in Table I. It may be noted that this compound is very reactive, rates being conveniently measurable at 0 and 12° as compared with 100–120° for the dichlorides, and with rates differing by six to eight orders of magnitude if the data on the chlorosulfone are extrapolated to 110°, or by ten to twelve orders of magnitude if the rates on the dichlorides are extrapolated down to 12°. Here we have a *cis* non-coplanar elimination proceeding at a very high rate, and with low activation energy, a result entirely consistent with predictions from the carbanion mechanism theory.

The carbanion mechanism may be detailed as



$$\mathrm{B\!: + H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B\!:\!H^+ + \;>\overset{\ominus}{C}{-}\overset{|}{\underset{|}{C}}X} \qquad (1)$$

$$\mathrm{>\overset{\ominus}{C}{-}\overset{|}{\underset{|}{C}}{-}X \xrightarrow{k_2} >C{=}C< + \;:\!X^{\ominus}} \qquad (2)$$



Some confusion apparently may exist as to when it may be experimentally distinguishable from the concerted process, where proton transfer, formation of the multiple bond and loss of halide ion occur simultaneously. It will not be distinguishable by deuterium-exchange studies or by studies of general base catalysis,[15] when $k_2 >> k_{-1}$. It will only be distinguishable when the sensitivities of the methods available for analysis of such results are consistent with the ratio k_{-1}/k_2. We see no reason to believe that it is more moderate[15] or conservative[9] to assume that all reactions in which substantial amounts of deuterium exchange are not observed or in which specific base catalysis is not found are concerted mechanisms, particularly in view of the body of evidence favoring a dual mechanism concept.

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Experimental

Materials Used.—*endo-cis*-2,3-Dichloronorbornane, m.p. 76–77°, and *trans*-2,3-dichloronorbornane, b.p. 43.5–44.5° (2.5 mm.), $n^{20}\mathrm{D}$ 1.5027, were prepared substantially as described by Roberts, Johnson and Carboni.[7] Our *trans* isomer was impure, however, and the kinetic work was performed with material that eliminated less than the theoretical amount of chloride ion under appropriate conditions. How this was corrected is described below under rate measurements. After all of the work had been completed, we succeeded in crystallizing the *trans* isomer, m.p. 5.5°. 2-*exo*-*p*-Toluenesulfonyl-3-chloronorbornane, m.p. 115–117°, was prepared by addition of *p*-toluenesulfenyl chloride to norbornene, followed by oxidation to the sulfone.[16]

1-Pentanol.—Commercial *n*-amyl alcohol contained significant amounts of chloride (1–2 mmoles/l.) even after distillation. For this reason *n*-amyl alcohol was treated with 1–2% of sodium and heated at reflux for 15 hours. It was then fractionally distilled and the fraction, b.p. 131–131.5° (630 mm.), was used. It showed no detectable halogen after this treatment.

Sodium 1-Pentoxide Solution.—About 11.5 g. of sodium, which had been cleaned first under toluene and then in 1-pentanol was dissolved in 1 liter of pure 1-pentanol. The solution was stored in a brown rubber-stoppered bottle and remained colorless for several months. Its titer was checked regularly and dropped slowly (less than 1% per month).

Measurements of Reaction Rates.—The rates at above 100° were run in sealed Corning 7280 alkali-resistant glass tubes, substantially as described previously,[3] except that the solvent was 1-pentanol. The thermostated baths appeared to hold constant temperature to ±0.05°, and temperatures recorded were checked against a National Bureau of Standards calibrated thermometer. The extent of reaction was followed by Volhard titration for chloride ion. Titration was accompanied by rapid stirring with a magnetic stirrer. This stirring helped in seeing the end-point clearly in the two-phase system. Calculations of rate were made in the usual graphical fashion,[3] and good lines (constant second-order rate constants) were obtained with the *endo-cis*-dichloride. However, the rate constants appeared to fall off rapidly with time with the *trans*-dichloride, and when

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(10) S. J. Cristol and D. D. Fix, THIS JOURNAL, **75**, 2647 (1953).

(11) L. C. Leitch and H. J. Bernstein, *Can. J. Research*, **28B**, 35 (1950).

(12) S. J. Cristol and A. Begoon, THIS JOURNAL, **74**, 5025 (1952).

(13) F. G. Bordwell and R. J. Kern, *ibid.*, **77**, 1141 (1955).

(14) J. Weinstock, R. G. Pearson and F. G. Bordwell, *ibid.*, **78**, 3468 (1956).

(15) J. Weinstock, R. G. Pearson and F. G. Bordwell, *ibid.*, **78**, 3473 (1956).

(16) The synthesis, proof of structure and elimination product study of this compound will be described in a paper by S. J. Cristol and G. D. Brindell.

the reaction was run for nine half-lives under pseudo first-order conditions (large excess of base), only 70–75% of the theoretical amount of chloride was produced. This amount did not appear to depend upon the concentration of alkali, so no base-insensitive transformation to a material which does not liberate chloride ion rapidly was involved. We suspect that our *trans* material was contaminated with the *cis-endo* isomer which, of course, is about 1/85 as reactive as the *trans* isomer. To correct for this, we attempted plots of our data feeding into our calculations various factors depending upon the percentage of *trans*-dichloride in the starting material. The data on all of the runs gave excellent straight lines when the value 71% was used to correct the initial concentration of dichloride and, of course, the extent of reaction as well. The rate constants in Table I are thus corrected.

As the solutions were made up at 20° and the reactions were run at 101 and 116°, the rate constants were further corrected for solvent expansion. The observed rate constants were multiplied by 1.09 and 1.11 at 101 and 116°, respectively.[17]

The rates at 12° were carried out in a thermostated water-bath in a room also held at 12°. Appropriate solutions of the chlorosulfone and base in 1-pentanol were equilibrated in the bath, were rapidly mixed in a volumetric flask, which was then filled to the mark with temperature-equilibrated 1-pentanol. The flask was shaken to mix the solution thoroughly and was then immersed in the bath. Samples were withdrawn every few minutes with a pipet having a tip which had been blown out to give rapid delivery, and these were run into an erlenmeyer flask containing 10 ml. of 2 *N* nitric acid. The runs at 0° were conducted in a water-ice bath in a room held at 5°. The pipets used for withdrawing samples were insulated by wrapping them with asbestos string and were stored in a long test-tube at 0°. In other respects the procedure followed was similar to that at the higher temperature.

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[17] A. Zander, *Ann.*, **224**, 56 (1884).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Mechanisms of Elimination Reactions. XIX. Elimination and Solvolytic Reactivities in Some Bicyclo[2,2,1]heptane and Bicyclo[2,2,2]octane Derivatives[1,2]

BY STANLEY J. CRISTOL AND ROBERT P. ARGANBRIGHT

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A striking lack of stereospecificity in elimination reactions involving bonds held in the rigid eclipsed positions available in boat-form cyclohexane molecules has been noted in the reaction of sodium hydroxide with the *cis* and *trans* isomers of 11-*p*-toluenesulfonyl-12-chloro-9,10-dihydro-9,10-ethanoanthracene. Both compounds reacted rapidly with alkali at 0 and 12°, the *cis* compound (*trans* elimination) reacting about three times as fast as the *trans* isomer. These results compared with those reported earlier for 11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene are well accommodated by the assumption that a carbanion is formed in the first step of the elimination reaction. Solvolysis rate constants for several β-chlorothioethers in bicycloheptane and bicyclooctane ring systems were determined in 85% ethanol at 116°. The extremely low reactivities and the minor difference in reactivity between *cis* and *trans* isomers demonstrate the lack of significant neighboring-group acceleration of solvolysis with groups held at rigid eclipsed bond angles.

Previous work[3] has shown that the normal preference for *trans* elimination disappears when groups are held rigidly in fixed positions such that *trans* coplanarity cannot be attained readily in the transition state for elimination. Evidence has been adduced to suggest that in these circumstances an alternative mechanism involving a carbanion is operative. It is the purpose of the present paper to supply further data in support of this postulate.

We have studied the rates of elimination of hydrogen chloride with sodium hydroxide from *cis*-(I) and *trans*-11-*p*-toluenesulfonyl-12-chloro-9,10-dihydro-9,10-ethanoanthracenes (II) to compare the rate constants and quantities of activation with those of the corresponding 11,12-dichlorides previously studied.[4] The rates were measured in a solvent consisting of 50% by volume of ordinary ethanol and 50% of dioxane. The rate data are given in Table I.

It will be noted that these compounds show extremely high reactivity toward elimination; the reactions proceed at quite rapid rates at 0 and 12°. These results may be contrasted with the results on the corresponding dichlorides,[4] which react at comparable rates at temperatures about 150° higher. If the data obtained on the dichlorides are extrapolated to 12°, the comparison of these values with the values given in Table I for the chlorosulfones indicate that substitution of a chlorine atom by a *p*-toluenesulfonyl group increases the rate of elimination by about 10 powers of 10. In addition, it should be noted that these compounds show little stereospecificity in the elimination reaction, *trans* elimination being favored over *cis* by a factor of only 3. It is of interest to note that in the two dichloride systems previously studied, that is, the dichlorodihydroethanoanthracenes[4] and the 2,3-dichloronorbornanes,[1] *cis* elimination was favored slightly over *trans*. In the present system, however, *trans* elimination is slightly favored over *cis*.

The striking lack of stereospecificity in this system, as well as in the systems previously studied, seems to us to be best explained on the basis that carbanion intermediates are involved and that a multiple-stage mechanism for elimination is utilized in these systems where bonds are rigidly held in eclipsed positions and a *trans* coplanar transition state is geometrically improbable. The tremendous increase in reactivity observed when an arenesulfonyl group replaces a chlorine atom in these systems may also be rationalized by the assumption that a carbanion mechanism is involved. We feel that the results given here lend additional support to the arguments given earlier.[1]

In addition it should be noted that a comparison

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[1] Previous paper in series: S. J. Cristol and E. F. Hoegger, THIS JOURNAL, **79**, 3438 (1957).

[2] This work was reported at the 130th meeting of the American Chemical Society in Atlantic City, New Jersey, September, 1956.

[3] References to previous work in this field are given in reference 1.

[4] S. J. Cristol and N. L. Hause, THIS JOURNAL, **74**, 2193 (1952).