chromatogram). The yield corresponds to 0.001 mole of material.

Anal. Calcd. for $C_{38}H_{24}N_6O_7$: C, 57.87; H, 3.06; N, 10.67. Found: C, 57.45; H, 3.19; N, 10.46.

The material remaining on the column was removed with methylene chloride and proved to be tri-(*p*-nitrophenyl)-carbinol, 0.64 g. (0.0016 mole) melting at 183–186°. This material had an infrared spectrum identical to that of authentic carbinol. A moderate amount of highly colored material remained on the column.

Miscellaneous Reactions of Tri-(*p*-nitrophenyl)-methyl Nitrate (I).—One gram of tri-(*p*-nitrophenyl)-methyl nitrate (I) was dissolved in 50 ml. of dry acetone. One gram of sodium iodide was added and the solution allowed to stand several minutes. The solution was flooded with water and the green tri-(*p*-nitrophenyl)-methyl radical precipitated from the aqueous iodine solution.

The solution of a few crystals of the nitrate ester I in a few drops of concentrated sulfuric acid resulted in the formation of an orange solution identical with that produced by the similar treatment of tri-(*p*-nitrophenyl)-carbinol. The ketone, 4,4′-dinitrobenzophenone gives a nearly colorless solution under the same circumstances.

HUNTSVILLE, ALABAMA

[CONTRIBUTION NO. 680 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

The Effects of γ-Methyl Substitution on the Rates of the Bimolecular Displacement and Elimination Reactions of Alkyl Halides[1]

BY V. J. SHINER, JR., M. J. BOSKIN AND M. L. SMITH

RECEIVED MARCH 24, 1955

Rate and olefin fraction data are presented which in conjunction with other information available in the literature allow the comparison of elimination rates in each branch as well as substitution rates for the series of compounds $(CH_3)_xCH_{3-x}$–CH_2–CHBr–CH_3 (with *x* equal to 3, 2, 1 and 0 with *ca.* 1 *N* sodium ethoxide in absolute ethyl alcohol). The displacement rate is slowed down progressively by increasing γ-methyl substitution with the extremes differing by a factor of 4.4. The rates of elimination in the left-hand branches vary over-all by a factor of about three and can be correlated with the number of C–H bonds available for hyperconjugation in a manner consistent with the Hughes-Ingold theory.[2] Increasing γ-methyl substitution also slows down the rate of elimination in the right-hand branch. The relation between these data and the problem of the effect of alkyl substitution on hyperconjugation is discussed.

The effects on the displacement and elimination reactions of alkyl halides, of branching alpha and beta to the displaced group have been systematically investigated, correlated and fairly well explained. The work of Brown and Fletcher[3] and of Hughes, Ingold and Shiner[4] shows that extensive branching at the γ-carbon atom also has a surprisingly large effect on the rate of unimolecular reactions of tertiary alkyl halides. For example, 2,4,4-trimethyl-2-chloropentane is solvolyzed around twenty times faster than *t*-butyl chloride to give a high proportion of 2,4,4-trimethylpentene-1 in violation of the Saytzeff rule. However, no studies on the effects of extensive γ-branching on the bimolecular reactions of alkyl halides have been reported. In this paper are reported new rate constants and olefin yields which with previously published data allow the tabulation of elimination rates in each branch as well as substitution rates for the series of compounds $(CH_3)_xCH_{3-x}$–CH_2–CHBr–CH_3 (with *x* equal to 3, 2, 1 and 0) with *ca.* 1 *N* sodium ethoxide in absolute ethyl alcohol. Therefore the step-by-step effect of γ-methyl substitution on the rates of typical bimolecular substitution and elimination reactions can be analyzed. In Table I are tabulated rate constants and olefin fractions for the reactions of 4-methyl-2-bromopentane and 4,4-dimethyl-2-bromopentane with sodium ethoxide in absolute ethanol. Corresponding values for isopropyl bromide are included for comparison.

TABLE I

REACTIONS WITH 1 *N* SODIUM ETHOXIDE IN ABSOLUTE ETHYL ALCOHOL

Compound	Temp., °C.	No. of points	K_2 (10^{-6} l./mole/sec.)	Std. dev.	Olefin fraction
Isopropyl bromide	25.00	12	2.957	0.003	0.640
Isopropyl bromide	35.00	12	10.59	.008	.677
Isopropyl bromide	45.00	12	37.91	.02	.704
Isopropyl bromide	55.00	12	116.2	.6	.731
4-Methyl-2-bromopentane	25.00	12	1.69	.01	.84
4,4-Dimethyl-2-bromopentane	35.00	10	4.72	.03	.87
4,4-Dimethyl-2-bromopentane	45.00	13	15.8	.2	.89
4,4-Dimethyl-2-bromopentane	55.00	14	47.6	.4	.88

Values of the Arrhenius parameters for the reactions of isopropyl bromide and 4,4-dimethyl-2-bromopentane, calculated from the data of Table I by the method of least squares, are tabulated in Table II.

TABLE II

ARRHENIUS PARAMETERS FOR REACTIONS WITH ETHOXIDE IONS IN ABSOLUTE ETHYL ALCOHOL[a]

Compound	E2 Log *A*	E2 E_a	S_N2 Log *A*	S_N2 E_a
Isopropyl bromide	12.42	24.8	10.18	22.0
4,4-Dimethyl-2-bromopentane	11.09	23.2	10.23	23.2

[a] Units of *A* are l./mole/sec. Std. deviations in log *A* are 0.01 and in E_a 0.2.

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[1] (a) Abstracted in part from a thesis submitted by M. J. Boskin to the Graduate School of Indiana University in partial fulfillment of the requirements for the M.A. degree. (b) Presented before the Division of Organic Chemistry at the 127th National Meeting of the American Chemical Society, Cincinnati, April 1, 1955. (c) Supported in part by the Petroleum Research fund of the American Chemical Society.

[2] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 434 ff.

[3] H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949).

[4] E. D. Hughes, C. K. Ingold and V. J. Shiner, Jr., *J. Chem. Soc.*, 3827 (1953).

TABLE III

PROPORTIONS OF ISOMERIC OLEFINS

(Analysis by infrared spectral data.)

Compound	Reaction	*cis*-2-Isomer	Total 2-Isomer	1-Isomer[d]
4,4-Dimethyl-2-bromopentane	E2 (NaOEt)	0.02[a,b]	0.79 ± 0.01	0.21 ± 0.01
4,4-Dimethylpentanol-2	Acid dehyd.	.02[a,b]	.85 ± .01	.15 ± .01
4-Methyl-2-bromopentane	E2 (NaOEt)	.04[a,c]	.81 ± .02	.19 ± .02
4-Methylpentanol-2	Acid dehyd.	0.26 ± 0.05[c]	.86 ± .05	.14 ± .05

[a] Maximum limits. [b] Analysis based on intensity of 14.14 μ band. [c] Analysis based on intensity of 13.89 μ band. [d] Analysis based on intensity of 6.06 μ band.

The method of kinetic analysis was essentially that described by Dhar, Hughes and Ingold[5] in which the reactions were carried out in sealed tubes in absolute ethanol with sodium ethoxide concentrations of about 1 molar. The over-all reaction was followed by titration of developing bromide ion using either the Volhard or a potentiometric method. The pseudo first-order rate constants and their standard deviations were determined by the method of least squares from the plot of log $(Br^-)_{inf.}/[(Br^-)_{inf.} - (Br^-)_t]$ *versus* time (t). The over-all second-order rate constant was obtained by dividing the pseudo first-order rate constant by the concentration of sodium ethoxide. After about ten to twenty half-lives the olefin fraction was estimated by the reaction of a sample with standard bromine solution. In order to determine the proportion of the isomeric olefins formed in the reaction of 4,4-dimethyl-2-bromopentane with sodium ethoxide, essentially pure 4,4-dimethylpentene-1 and *trans*-4,4-dimethylpentene-2 were prepared. The infrared spectra of these materials agree well with those already published.[6a,b] The published spectrum of pure *cis*-4,4-dimethylpentene-2[6c] shows a strong band at about 14.14 μ while those of the *trans*-2-isomer[6b] and the 1-isomer show no absorption in this region. Calculations based on the intensity of the peak at 14.14 μ showed that our *trans*-2-isomer contained not more than 2% of the *cis*-isomer. Synthetic mixtures of known concentration of the *trans*-2-isomer and the 1-isomer were made and their absorption spectra compared with that of the mixture of olefins isolated from a reaction between 4,4-dimethyl-2-bromopentane and alcoholic sodium ethoxide. Calculations based on the intensity of the band at 6.06 μ showed that the reaction mixture contained 79 ± 1% of the 2-isomer and 21 ± 1% of the 1-isomer. Calculations based on the intensity of the small band at 14.11 μ indicated that there was no more than 2% of the *cis*-2-isomer in the reaction mixture. The dehydration of 4,4-dimethylpentanol-2 gave a mixture of olefins containing 85 ± 1% of the 2-isomer of which a maximum of 2% is the *cis*-2-isomer.

The proportion of the two olefins obtained in the reaction of 4-methyl-2-bromopentane with sodium ethoxide was determined by isolating the mixture of olefins from the reaction and comparing its infrared spectrum with that of pure 4-methylpentene-1, obtained in this Laboratory and those of 4-methylpentene-1, *cis*- and *trans*-4-methylpentene-2 previously published.[6d,e,f] A strong absorption at 13.89 μ is characteristic of the *cis*-4-methylpentene-2[6d] and absent in the *trans*[6e] and 1-isomers.[6f] Our sample of the 1-isomer showed the same spectrum as that already published with no band at 13.89 μ. Calculations based on the intensity of the band at 13.89 μ in the kinetic mixture of olefins indicate the presence of less than 4% of the *cis*-isomer. Calculations based on the intensity of the 6.06 μ band, characteristic of the 1-isomer and absent in the *trans*-isomer, show the mixture to contain 19 ± 2% of 4-methylpentene-1. Similar calculations show that the product from the acid-catalyzed dehydration of 4-methylpentanol-2 is a mixture of all three olefins in the following proportions: *trans*-2, 60 ± 5%; *cis*-2, 26 ± 5%; 1-isomer, 14 ± 5%. The results of these olefin analyses are given in Table III. To determine the extent, if any, of olefin isomerization during the preparation of the kinetic olefin mixtures, both pure 4,4-dimethylpentene-1 and 4-methylpentene-1 were subjected to the reaction conditions and re-isolated. The infrared spectra of the recovered materials show that they had undergone no isomerization.

The data in Tables I and II can be combined with other similar data already in the literature[5] for 2-bromobutane and 2-bromopentane to give as in Table IV the rate constants for each of the composite reactions for each of the compounds in the series under consideration.

TABLE IV

RATE CONSTANTS FOR REACTIONS OBSERVED IN *ca.* 1 *N* ALCOHOLIC SODIUM ETHOXIDE AT 25°

Compound	*K* SN2	*K* (left) E2 total	*K* (left) E2 Per H	*K* (right) E2 total	*K* (right) E2 Per H
$CH_3CHBrCH_3$	1.06	0.94	0.31	0.94	0.31
$CH_3CH_2CHBrCH_3$[a]	0.75	2.82	1.41	.65	.22
$CH_3CH_2CH_2CHBrCH_3$[a]	.67	1.96	0.98	.80	.26
$(CH_3)_2CHCH_2CHBrCH_3$	.27	1.15	.57	.27	.09
$(CH_3)_3CCH_2CHBrCH_3$[b]	.17	0.92	.46	.24	.08

[a] M. L. Dhar, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2058 (1948). [b] Obtained by extrapolation of an Arrhenius plot.

It is seen that the substitution rates fall steadily in the series as the number of γ-methyl groups is increased. The extent to which this is due to the inductive effect must be small after the second member of the series is passed because the effect gets somewhat larger even though the additional methyl substitution is further removed by one more carbon atom. Table II shows that the log *A* factors are nearly the same for the substitution

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(5) M. L. Dhar, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2058 (1948).

(6) Catalogue of Infrared Spectral Data, American Petroleum Institute: (a) No. 1063; (b) No. 1084; (c) No. 1082; (d) No. 929; (e) No. 931; (f) No. 710.

reactions of isopropyl bromide and of 4,4-dimethyl-2-bromopentane while the higher activation energy for the latter accounts almost exclusively for its slower substitution rate. Steric compressions in the transition state for the reaction of the more highly branched compound must account for a good part of this activation energy difference. It seems strange therefore that its log *A* factor is not lower than that for isopropyl bromide. Apparently activation for the reaction of 4,4-dimethyl-2-bromopentane does not restrict any vibrations or rotations not already restricted in its initial state or not similarly restricted in the substitution reaction for isopropyl bromide. This analysis suggests then that the third and fourth members of the series in Table IV differ in rate of reaction from *sec*-butyl bromide (2nd member) because of a steric entropy effect and not because of a steric energy effect.[7] This would predict, although the data are not available for comparison, that members 2, 3 and 4 would have almost the same activation energy and that the log *A* factors would account for most of the observed rate differences. This argument is supported by the examination of scalar models of the transition states for the displacement of bromide by ethoxide in 4-methyl-2-bromopentane and in 4,4-dimethyl-2-bromopentane. The point to be noticed is that until all three hydrogen atoms on the γ-carbon atom are replaced by methyl groups the C_β–C_γ bond can still be rotated so that there is little interference between the γ-methyl groups and the incoming or departing groups. This implies that each of the first two methyl groups substituted would put an additional restriction on the conformation of the transition state but would not increase its energy. When the third γ-methyl group is substituted there are more energetically equivalent conformations, corresponding to different phases of rotation about the C_β–C_γ bond, but all of these should have higher energy content due to compressions between the γ-methyl groups and the incoming and departing groups.

The rate constants for elimination in the left-hand branches, given in Table IV, show a smooth correlation with the number of C–H bonds available for hyperconjugation with the developing double bond. The rates in the series vary as follows: 0.31, 1.41, 0.98, 0.57 and 0.46 per hydrogen atom as the number of hyperconjugating C–H bonds changes 3, 6, 5, 4 and 3, respectively. This is in accord with the theory of Hughes and Ingold.[2] However, this is the first time that it has been shown that the ability of alkyl groups to promote this type of elimination in a neighboring bond varies in a hyperconjugative manner through the complete series from methyl to *t*-butyl. It has been shown in this paper that elimination in the left-hand branches of the last two members of the series gives 96 to 98% of the *trans* olefin. Since it has been reported[5] that the bimolecular elimination in the inside branch of 2-bromobutane gives almost exclusively *trans*-2-butene it appears certain that such is also the case with 2-bromopentane and that no statistical factor based on such considerations could appreciably change the nature of the series as outlined above.

The differences in the Arrhenius parameters for elimination for isopropyl bromide and 4,4-dimethyl-2-bromopentane (Table II) are not simply explainable because they relate to a composite of the elimination processes in the two branches in each case. However, it is reasonable that the energy of activation for the latter is lower because elimination in the central branch should be stabilized by additional alkyl substitution. Likewise its frequency factor should also be lower because of the statistical effect that there are only two hydrogens in this branch to be eliminated while there are six equivalent ones in isopropyl bromide. In addition the formation of the *trans* olefin of the highly branched material should involve relatively less probability, less entropy of activation and therefore a smaller A factor.

The rate constants for elimination in the right-hand (or "outside") branches are of interest with regard to the effect of alkyl substitution on hyperconjugation when the number of hyperconjugating C–H bonds remains constant. In this series the number of such bonds changes from three in the first member to two in the second and thereafter remains constant. In accord with the hypothesis of hyperconjugative control the rate for the first member is highest, but beyond this there are significant differences in the rest of the series. Excepting the third member of the series which is slightly out of line, the general trend is a decrease in rate as the hydrogen atoms beta to the developing double bond are replaced by methyl groups. The substituent groups fall in the following order in promoting elimination: *n*-propyl > ethyl > isobutyl > neopentyl. Except for the fact that *n*-propyl is out of line this is very similar in relative magnitude as well as direction to the effects that Berliner and Berliner[8] observed these substituent groups to have on the rates of bromination of benzene. Robertson, Heyes and Swedlund[9] similarly observed that neopentylethylene is brominated at about one-tenth the rate of *n*-butylethylene. Several different explanations have been proposed to explain this type of phenomena: Steric inhibition of solvation (either at a reaction center as remote as six atoms removed, or at nearer centers bearing partial charges by virtue of electromeric transmission),[10] inductive effect on hyperconjugation,[9] so-called second-order hyperconjugation,[8] steric inhibition of hyperconjugation,[11] and direct steric effect.[12]

In our opinion the data which bear on this problem are still too meager to allow a definite choice to be made between the various conceivable

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[7] N. Ivanhoff and M. Magot, *J. chim. phys.*, **47**, 1950 (1914).

[8] E. Berliner and F. Berliner, THIS JOURNAL, **73**, 222 (1950).

[9] P. W. Robertson, J. K. Heyes and B. E. Swedlund, *J. Chem. Soc.*, 1014 (1952).

[10] C. C. Price and W. J. Belanger, THIS JOURNAL, **76**, 2682 (1954).

[11] G. Baddeley and M. Gordon, *J. Chem. Soc.*, 2190 (1952).

[12] H. C. Brown, personal communication. Professor Brown also pointed out that the elimination rates in the left-hand (or inside) branches could be correlated with the bulkiness and presumably the steric effect of the β-situated alkyl group. Thus the rate trend alone does not serve to distinguish between steric and hyperconjugative control.

explanations. It is hoped that further work now in progress in this Laboratory will contribute toward the solution of this and several other related general problems pertaining to hyperconjugation.

Experimental

Kinetic Procedure.—The kinetic method, the analyses for bromide ion and for olefin have been described previously.[13]

All bath temperatures were set by Beckmann thermometers standardized in the baths at the exact temperature desired against the same platinum resistance thermometer and Mueller bridge arrangement, sensitive to a few thousandths of a degree. The temperature accuracy, not limited by the calibration standard should be of the order of ±0.01° or less.

For the isopropyl bromide kinetic runs the bromide ion was extracted in an aqueous solution and titrated with silver nitrate solution directly using a potentiometer arrangement with a silver electrode as the indicator. The details of this procedure will be published later.

Preparation of Organic Compounds.—A sample of 62.5 g. (0.55 mole) of 4,4-dimethyl-2-pentanone,[14] b.p. 124–125° (760 mm.), n^{25}D 1.4018, was added slowly to a slurry of 7.6 g. (0.2 mole) of lithium aluminum hydride in 600 ml. of dry ether under dry nitrogen. The excess hydride was decomposed with water and the mixture was poured on 500 ml. of ice-cold 10% sulfuric acid. The ether layer and the ether extracts of the water layer were combined, washed, dried with anhydrous potassium carbonate and distilled. 4,4-Dimethyl-2-pentanol, 40 g. (0.34 mole), was collected at 137–138° (751 mm.); n^{25}D 1.4168; yield 62%.

4,4-Dimethyl-2-bromopentane, 24.9 g. (0.14 mole), b.p. 59.3–59.8° (33 mm.), n^{25}D 1.4439, was prepared by the slow addition of excess gaseous hydrogen bromide to 42.5 g. (0.37 mole) of 4,4-dimethyl-2-pentanol at about 60°.

4-Methyl-2-pentanol, 41.2 g. (0.41 mole), b.p. 132°, was prepared following the usual Grignard technique from 137 g. (1.0 mole) of isobutyl bromide and 50 g. (1.1 moles) of acetaldehyde, b.p. 20.5–21°. 4-Methyl-2-bromopentane, 45 g. (0.27 mole), b.p. 33° (mm.), was prepared from 41 g. (0.41 mole) of the corresponding alcohol and gaseous hydrogen bromide.

4,4-Dimethylpentene-1, 105 g. (1.07 mole), b.p. 71.0–71.8° (755 mm.), n^{25}D 1.3902, was prepared by the addition of 5.0 moles of *t*-butylmagnesium chloride to an ice-cold solution of 605 g. (5.0 moles) of allyl bromide in ether. This material was redistilled in a 75-plate Wheeler concentric tube column and separated into 14 fractions. The infrared spectra of fractions 6 to 12, recorded parallel to one another on the same chart, using a Perkin–Elmer Model 21 infrared recording spectrophotometer, showed no differences between fractions. A cooling curve taken on a portion of the mixture of these fractions with a two-junction copper–constantan thermocouple calibrated at four points showed f.p. (initial) −137.62°, f.p. (half-frozen) −137.70°.

4,4-Dimethylpentene-2, b.p. 76.7–76.8°, n^{25}D 1.3960, was prepared by the dehydration of 4,4-dimethyl-2-pentanol and was purified by distillation through the 75-plate concentric tube column. The infrared spectra of successive fractions again showed a good "flat" and a cooling curve on the fraction used gave f.p. (initial) −118.86°; f.p. (half-frozen) −119.04°.

4-Methylpentene-1 was prepared by the addition of isopropylmagnesium bromide to allyl bromide and was purified by distillation through a 40 × 0.9 cm. column packed with phosphorbronze screen helices and equipped with a partial take-off head. All other organic compounds used, except solvents, were carefully purified by distillation through a 50 × 1.0 cm. vacuum-jacketed column packed with $^{3}/_{32}''$ glass helices and equipped with a partial take-off head.

Preparation of Kinetic Mixture of Olefins.—A sample of 9.7 g. (0.54 mole) of 4,4-dimethyl-2-bromopentane was thoroughly mixed with 100 ml. of about 1 *N* sodium ethoxide in absolute ethanol and allowed to react at 45° for about ten half-lives. The contents were then mixed in a separatory funnel with 800 ml. of water and fifty ml. of fractionally distilled petroleum ether (b.p. 28°). The organic layer was separated and the aqueous layer was washed with two more portions of petroleum ether. The combined petroleum ether extracts were dried over anhydrous potassium carbonate and most of the petroleum ether was removed through a 40 × 0.9 cm. total reflux, partial take-off column packed with phosphorbronze screen helices. The residue was then distilled through a 20 × 0.6 cm. straight-tube column and 3.0 g. (0.031 mole) of olefin was collected, b.p. 69–78°. The olefin composition of this sample was determined by comparison of infrared spectrum with that of synthetic mixtures of known concentration.

BLOOMINGTON, INDIANA

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(13) V. J. Shiner, Jr., THIS JOURNAL, **74**, 5285 (1952).

(14) W. A. Mosher and J. C. Cox, *ibid.*, **72**, 3701 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Reaction of Silver Nitrite with Secondary and Tertiary Alkyl Halides[1,2]

BY NATHAN KORNBLUM, ROBERT A. SMILEY, HERBERT E. UNGNADE, ALAN M. WHITE, BERNARD TAUB AND STEPHEN A. HERBERT, JR.

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Treatment of secondary halides with silver nitrite gives nitroparaffins in *ca.* 15% yields. The reaction of tertiary halides with silver nitrite is even less useful as a means of preparing nitroparaffins (0 to 5% yields). The complex mixtures produced have been shown to contain, in addition to the anticipated nitroparaffins and nitrite esters, olefins, nitrate esters and adducts of olefins with oxides of nitrogen.

In the preceding paper[3] it was shown that the reaction of primary bromides and iodides with silver nitrite gives excellent yields of primary nitroparaffins. The present study is concerned with the utility of this reaction for the synthesis of secondary and tertiary nitro compounds. Furthermore, our interest in the mechanism of these reactions has led us to determine how much alkyl nitrite is formed.

It transpires that when secondary and tertiary halides react with silver nitrite a rather complex mixture is produced. In addition to the anticipated nitroparaffin and nitrite ester, a number of other compounds have been isolated and identified.

Secondary Halides.—As is clear from the data of Table I, the yields of nitro compounds obtained on treating secondary bromides and iodides with silver

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[1] Paper VI in the series "The Chemistry of Aliphatic and Alicyclic Nitro Compounds."

[2] This research was supported by the United States Air Force under Contract No. AF 18(600)-310 monitored by the Office of Scientific Research, Air Research and Development Command.

[3] N. Kornblum, B. Taub and H. E. Ungnade, THIS JOURNAL, **76**, 3209 (1954); *cf.* also C. W. Plummer and N. L. Drake, *ibid.*, **76**, 2720 (1954).