Time, min.	Mole per cent. of original hydrocarbon 3-Ethyl-pentane	Triethyl-carbinol	3-Pentanone	Propionic acid
30	..	39	52	11
35	..	30	54	13
40	..	15	56	16
45	..	6	58	18
50	..		59	21
55	..		59	24
60	..		60	27

In order to obtain some check on this indirect method a larger scale oxidation was carried out and the mixture analyzed at an early stage by fractional distillation. A mixture of 50 cc. of 2 *N* aqueous sodium dichromate, 50 cc. of sulfuric acid and 450 cc. of glacial acetic acid was cooled to 8°. 3-Ethylpentane (5.0 g., 0.050 mole) was added and the mixture immersed in a cold water-bath and stirred for ten minutes during which time the temperature rose to 14°. The reaction was stopped after 10 minutes by adding about 300 g. of ice at once and 85 g. of sodium carbonate as fast as evolution of carbon dioxide would permit. After standing at room temperature overnight the solution was filtered from precipitated sodium sulfate, and both solid and filtrate were extracted several times with methylene chloride. The combined extracts (600 cc.) were washed with water and the solvent removed by fractionation. When the volume of product and solvent was reduced to 25 cc., 2 cc. of nitrobenzene was added and distillation continued on a concentric tube column. The following fractions were collected: 92–94°, 0.65 cc.; 102–104°,[12] 1.9 cc.; 141–143, 2.8 cc.

An infrared spectrum of the fraction boiling from 141 to 143°, except for a small carbonyl peak at 5.85 μ, was identical with that for an authentic sample of triethylcarbinol.

To check the possibility of induced oxidation, 84 mg. of $MnSO_4$ was added to the aqueous dichromate solution prior to mixture with the remaining reagents. The oxidation rate for 90 minutes was the same within experimental error as that for mixtures without added manganous ion.

Oxidation of Triethylcarbinol.—The oxidation of 0.270 g. of alcohol was carried out by the usual procedure. Analysis for consumption of dichromate at different times gave the following data.

Time, min.	Mole Cr_2O_7 per mole alcohol	Mole ketone per mole alcohol	Time, min.	Moles Cr_2O_7 per mole alcohol	Mole ketone per mole alcohol
0	0	0	20	0.48	0.35
2	0.05	0.08	30	.65	.46
3	.11		45	.90	.53
5	.20	.15	60	1.09	.60
10	.27	.24	75	1.18	.64
15	.38	.32	90	1.27	

Oxidation of Camphane.—An oxidation mixture consisting of 20 cc. of sulfuric acid, 180 cc. of acetic acid and 20 cc. of 2 *N* sodium dichromate was cooled to 8° in an ice-bath. Camphane (0.93 g., 0.0067 mole) was added and the temperature of the mixture maintained at 10–12°. After five hours a 5-cc. aliquot was titrated, showing that 0.0022 mole of dichromate had been consumed. The reaction was stopped by diluting with ice-water to 500 cc., and the mixture was extracted five times with 50-cc. portions of dichloromethane. The combined extracts were washed with water, dilute sodium carbonate, and water, and finally with one 100-cc. and two 50-cc. portions of concentrated sulfuric acid.

The yellow acid extracts were poured into 500 cc. of ice and water. The turbidity of the dilute acid solution was removed by washing with two 15-cc. portions of dichloromethane. This solvent was evaporated to leave 0.5 g. of soft brown crystals, which were sublimed at reduced pressure. The sublimate, which weighed 210 mg., melted at 155–160°, recrystallized m.p. 175–177°.[13] *Anal.* Calcd. for $C_{10}H_{16}O$: C, 78.88; H, 10.60. Found: C, 78.48; H, 10.53.

A 10-mg. sample of the product was introduced into 2 ml. of the usual oxidation mixture. After four hours at room temperature no perceptible darkening had taken place. The product gave a 2,4-dinitrophenylhydrazone, m.p. 173–174°, mixed m.p. with *dl*-camphor 2,4-dinitrophenylhydrazone[14] 140–145°. *Anal.* Calcd. for $C_{16}H_{20}N_4O_4$: C, 57.83; H, 6.02. Found: C, 57.62; H, 6.15. A semicarbazone of this product decomposed at 200° with KOH yielded a hydrocarbon, m.p. 153–155°, which gave no depression in melting point with an authentic sample of *dl*-camphane.

Acknowledgment.—We wish to express our gratitude for the generous support given this work by the Office of Naval Research. We are also indebted to Dr. Bernhard Witkop of the National Institutes of Health for the infrared data.

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[12] This fraction was converted quantitatively into the 2,4-dinitrophenylhydrazone of diethyl ketone, m.p. and mixed m.p. 156°.

[13] Epicamphor m.p. 182°, Y. Asahina and M. Ishidate, *Ber.*, **67B**, 71 (1934).

[14] R. Shriner and R. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., third edition, 1948, p. 265.

WASHINGTON, D. C.

[CONTRIBUTION FROM SOCONY MOBIL LABORATORIES, A DIVISION OF SOCONY MOBIL OIL COMPANY, INC., RESEARCH AND DEVELOPMENT DEPARTMENT]

The Abstraction of Hydrogen Atoms from Liquid Hydrocarbons by *t*-Butoxy Radicals

BY A. L. WILLIAMS, E. A. OBERRIGHT AND J. W. BROOKS

RECEIVED AUGUST 4, 1955

Removal of hydrogen atoms from liquid hydrocarbons by *t*-butoxy radicals has been investigated. The reactivities of hydrogen atoms have been measured by the rate of formation of *t*-butyl alcohol relative to the rate of decomposition of *t*-butoxy radicals to acetone. Ratios of the specific rate constants for the hydrogen abstraction reaction to the specific rate constant for *t*-butoxy radical decomposition have been calculated from the molar ratios of *t*-butyl alcohol to acetone obtained experimentally. The specific rate constant ratios permit a comparison of the reactivities of different types of hydrogen atoms for the abstraction process.

The rates at which hydrogen atoms of various types are removed from gaseous hydrocarbons by methyl radicals have been investigated by Trotman-Dickenson and Steacie.[1] Rate constants (relative to the combination of methyl radicals) characteristic of various types of hydrogen atoms in alkanes were calculated by considering the hydrogen atoms as though they were present in separate molecules in a multicomponent mixture. Application of this treatment to liquids is complicated by the increased probability of combination of methyl radicals to yield ethane.[2]

t-Butoxy radicals permit measurement of the rate of abstraction of hydrogen atoms from liquid hydrocarbons. The rate measurements are rela-

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[1] A. F. Trotman-Dickenson, J. R. Birchard and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 163 (1951).

[2] A. F. Trotman-Dickenson, *Quart. Rev.*, **7**, 198 (1953).

tive to the decomposition of *t*-butoxy radicals. This method has been used by Raley, Rust and Vaughan.[3] Hydrogen atoms of any given type are removed at a rate which depends upon the accessibility of these atoms, and upon the nature of the abstracting radical.[4]

In this study of liquid hydrocarbons, *t*-butoxy radicals were selected because they are easily generated thermally from di-*t*-butyl peroxide and lead to stable products which are easily identified.

$$(CH_3)_3CO\cdot + RH \xrightarrow{k_h} (CH_3)_3COH + R\cdot \qquad (1)$$

$$(CH_3)_3CO\cdot \xrightarrow{k_d} (CH_3)_2CO + CH_3\cdot \qquad (2)$$

The ratio of *t*-butyl alcohol to acetone, determined by infrared spectrophotometry, is the ratio of *t*-butoxy radicals abstracting hydrogen to those decomposing (k_h/k_d). Rust and co-workers have investigated the fate of the radicals produced.[5] Side reactions cannot affect the measured ratio of butanol to acetone unless they make or destroy alcohols or ketones or change the hydrocarbon structures. Removal of hydrogen from alcohols by radicals occurs at carbon atoms, rather than at hydroxyl groups, and would not influence the analysis for alcohol.[6] Gross changes in the hydrocarbon are minimized by working with saturated hydrocarbons in large excess. Hydrocarbons were selected with the objective of obtaining specific rates of abstraction (relative to *t*-butoxy radical decomposition) for individual hydrogen atom types.

Experimental

Materials.—Di-*t*-butyl peroxide (Matheson) analyzed 99+% peroxide. The butylbenzenes (Phillips, pure grade) were likewise of 99 + % purity. Dimethylpentanes, prepared at these Laboratories, were shown to be of 99% purity by infrared spectra. These materials, and all other hydrocarbons (Eastman Kodak Co.), were freed of peroxides by percolation over silica gel (Davison commercial grade) prior to reaction. The purified reactants were stored under nitrogen. Infrared spectra showed the percolated hydrocarbons to be free of carbonyl and hydroxy compounds, as well as olefins. Iodometric analyses showed peroxides to be absent.

Method.—Solutions of precisely known concentration (*ca.* 5 wt. %) of di-*t*-butyl peroxide in each hydrocarbon were prepared. After introduction of 10 ml. of the solutions into glass bomb tubes (20-ml. capacity), the bombs were cooled with Dry Ice in acetone, evacuated and sealed. The tubes were immersed for 7.5 hr. in an oil-bath at 135° (±1°). Then the reaction was immediately quenched by plunging the ampules into water. The contents of the tubes were analyzed within 24 hr. Bomb tubes were not opened until preparations had been made for the analyses. Di-*t*-butyl peroxide was determined by the method of Dickey and coworkers.[7] Analyses for butanol and acetone were performed by the infrared spectrometric procedure developed by Raley, Rust and Vaughan.[3] Weight percentages were obtained by comparison of the unknowns against standards of known concentration in the same hydrocarbon.

Discussion

To reduce abstraction of hydrogen atoms from molecules other than those of hydrocarbon the initial concentration of di-*t*-butyl peroxide was kept small.[8] This maintains the hydrocarbon concentration at a high, nearly constant level so that reaction (1) assumes first order kinetics.

The rate of hydrogen abstraction is given by

$$r_1 = k_h[BuO\cdot]\,[RH]$$

and the rate of *t*-butoxy radical decomposition is given by

$$r_2 = k_d[BuO\cdot]$$

The ratio of rates is

$$\frac{r_1}{r_2} = \frac{k_h}{k_d}\,[RH] \qquad (3)$$

The ratio r_1 to r_2 is obtained from the molar concentrations of *t*-butyl alcohol and acetone.

Reaction (2) could be other than first order if an unknown molecular species is present which promotes *t*-butoxy radical decomposition. If the concentration of *t*-butoxy radicals is increased, by employing a larger initial concentration of peroxide, the concentration of the hypothetical promoter for *t*-butoxy radical decomposition would also be increased. The reaction would then be greater than first order, and the ratio of butanol to acetone would decrease. However, when solutions of di-*t*-butyl peroxide of 2.99, 4.00 and 6.03 wt. % in toluene at 140° were 50% decomposed ratios of 1.86, 1.88 and 1.84, respectively, were obtained. The agreement between these ratios also shows that decomposition of *t*-butoxy radicals is not occurring at a limited number of active centers on the walls. In this case the ratio of butanol to acetone would increase with increasing *t*-butoxy radical concentration. In fact surface catalyzed decomposition of *t*-butoxy radicals is negligible here since tripling the surface by the use of capillary tubes did not alter the measured ratios of butanol to acetone. It is therefore concluded that reaction (2) is first order.

The ratios of butanol to acetone found in various hydrocarbons are listed in Table I. Low values

TABLE I

RELATIVE REACTION RATES OF HYDROCARBONS WITH *t*-BUTOXY RADICALS

Hydrocarbon	Initial concn. peroxide (wt. %)	% Peroxide left after 7.5 hr. at 135°	% of peroxide accounted for	Butanol found (wt. %)	Acetone found (wt. %)	Butanol–acetone molar ratio
Benzene	5.04	35	74	0.03	1.54	0.015
t-Butylbenzene	5.04	30	99	1.14	1.86	0.48
Mesitylene	4.96	32	98	2.94	0.31	7.4
1-Methylnaphthalene	4.75	23	88	2.46	0.61	3.2
2-Methylnaphthalene	4.95	25	103	2.57	1.15	1.8
n-Hexadecane	4.97	33	91	2.36	0.32	5.8
Cyclohexane	4.97	44	87	2.04	0.09	18
Ethylbenzene	4.98	28	102	3.07	0.53	4.5
Tetralin	5.08	30	99	3.37	0.11	24
2,3-Dimethylpentane	5.02	42	87	1.87	0.32	4.6
Decalin	4.98	40	93	2.56	0.11	18
Isopropylbenzene	4.80	..	101	3.64	0.85	3.4

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[3] J. H. Raley, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **70**, 1336 (1948).

[4] H. C. McBay, O. Tucker and A. Mulligan, *J. Org. Chem.*, **19**, 1003 (1954).

[5] F. F. Rust, F. W. Seubold and W. E. Vaughan, THIS JOURNAL, **70**, 95 (1948).

[6] W. H. Urry, F. W. Stacy, O. O. Juveland and C. H. McDonnell, *ibid.*, **75**, 250 (1953).

[7] F. H. Dickey, J. H. Raley, F. F. Rust, R. S. Treseder and W. E. Vaughan, *Ind. Eng. Chem.*, **41**, 1673 (1949).

[8] G. O. Pritchard, H. O. Pritchard and A. F. Trotman-Dickenson *J. Chem. Soc.*, 1425 (1954).

Table II

Relative Reaction Rates of Hydrogen Atoms with *t*-Butoxy Radicals

Hydrogen atom type	Calcd. from	k_1/k_d at 135°	Relative rate
Benzene	Benzene	0.0003	0.03
Primary unactivated	*t*-Butylbenzene	.0099	1.0
Primary activated by phenyl	Mesitylene	.121	12.2
Primary activated by 1-naphthyl	1-Methylnaphthalene	.17	17
Primary activated by 2-naphthyl	2-Methylnaphthalene	.098	9.9
Secondary unactivated	*n*-Hexadecane *t*-Butylbenzene	.069	7.0
Secondary unactivated cyclohexyl	Cyclohexane	.20	20
Secondary activated by phenyl	Ethylbenzene *t*-Butylbenzene	.32	32
Secondary cyclohexyl, activated by benzene	Tetralin Cyclohexane	.75	76
Tertiary unactivated	2,3-Dimethylpentane *n*-Hexadecane *t*-Butylbenzene	.28	28
Tertiary activated by phenyl	Isopropylbenzene *t*-Butylbenzene	.50	51

for the "peroxide accounted for" may arise through side reactions of *t*-butoxy radicals, but this would not affect the competition between reactions (1) and (2).

The methyl hydrogen atoms in 1-methylnaphthalene are more reactive than those of the 2-isomer. This would be predicted from the greater number of resonance forms of the radical from 1-methylnaphthalene.

A comparison of cyclohexane with *n*-hexadecane shows the greater reactivity of the cyclic secondary hydrogen atoms. Close comparisons of reactivities of hydrogen atom types cannot be made from ratios of butanol to acetone alone since these ratios depend upon hydrogen atom concentrations.

If each hydrogen type in a molecule is considered a potential reactant, then

$$\frac{r_1}{r_2} = \frac{[\mathrm{RH}]}{k_\mathrm{d}}\,(k_1Z_1 + k_2Z_2 + k_3Z_3 + \ldots) \tag{4}$$

where Z_1, Z_2, etc., represent the number of hydrogen atoms of a given type per molecule. When the hydrocarbon contains only one type of hydrogen, equation 4 becomes

$$\frac{k_1}{k_\mathrm{d}} = \frac{r_1}{r_2Z_1[\mathrm{RH}]} \tag{5}$$

The k_1/k_d ratios have been calculated, using equation 5, for a series of hydrogen atom types from data obtained with hydrocarbons containing only one type of hydrogen atom. These values can then be substituted in equation 4 to obtain values of k_2/k_d, k_3/k_d, etc., using appropriate hydrocarbons, since the decomposition of *t*-butoxy radicals has been found to be first order. If this is true in all of the solvents employed, k_d is of equal value in each hydrocarbon.

Since benzene hydrogen atoms have a very low reactivity, their contributions to the k_1/k_d ratios for alkylbenzenes were neglected. For these calculations compounds were selected which contain a high percentage of the hydrogen atom type under investigation. Molarities of the hydrocarbons were calculated by extrapolation of the densities to 135°. The relative rates of abstraction, compared to that of a primary unactivated hydrogen of an assigned value of 1, are listed in Table II.

The trend in the rates of abstraction is like that found in the reaction of methyl radicals with gaseous hydrocarbons.[2] Reaction of *t*-butoxy radicals with liquid alkanes gives the sequence: primary, 1; secondary, 7; tertiary, 28. Hydrogen atoms activated by a benzene ring are more reactive but preserve the same ordering: primary, 12; secondary, 32; tertiary, 51.

Secondary hydrogen atoms of tetralin activated by the benzene ring, as well as by the alicyclic ring, were the most active type found. The high ratio of butanol to acetone found for *n*-hexadecane is due to the great concentration of secondary hydrogen atoms; the unactivated secondary hydrogen atom is not very readily removed by the *t*-butoxy radical.

Where unknown resonance or steric factors are not involved, the rate constant ratios of Table II can be used to calculate ratios of butanol to acetone for untested compounds at 135°. Substitution of the appropriate values in equation 4 led to the calculated ratios in Table III.

Table III

Calculated Molar Ratios of Butanol to Acetone

Hydrocarbon	Initial concn. peroxide (wt. %)	% Peroxide left after 7.5 hr. at 135°	% of peroxide accounted for	Butanol found (wt. %)	Acetone found (wt. %)	Butanol-acetone molar ratio	
						Found	Calcd.
o-Xylene	4.96	26	98	2.97	0.48	4.9	5.0
m-Xylene	4.99	28	98	2.92	.46	5.0	4.9
p-Xylene	4.97	29	95	2.86	.37	6.1	4.9
Toluene	4.71	28	99	2.35	.80	2.3	2.8
sec-Butylbenzene	5.03	27	99	2.84	.65	3.4	3.8
n-Butylbenzene	5.02	30	104	3.16	.49	5.1	5.1
2,4-Dimethylpentane	4.98	33	86	2.10	.45	3.7	4.5

The results are generally in good agreement with the ratios of butanol to acetone obtained by experiment. The low ratio of butanol to acetone found for 2,4-dimethylpentane may arise from the greater steric hindrance encountered by *t*-butoxy radicals in approaching the tertiary hydrogen atoms of this hydrocarbon. Taft has shown that these hydrogen atoms should be more hindered than the tertiary hydrogens of 2,3-dimethylpentane.[9] The high experimental value for *p*-xylene may be a result of the small steric hindrance in *p*-xylene combined with the resonance stabilization of the *p*-xylyl radical.

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PAULSBORO, NEW JERSEY

[9] Robert W. Taft, Jr. (Pennsylvania State University); presented at a seminar, University of Pennsylvania, February, 1955.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Mechanism of Halide Reductions with Lithium Aluminum Hydride. III. Reduction of α-Chloro Acids and Esters[1,2]

BY ERNEST L. ELIEL, CAROLYN HERRMANN[3] AND JAMES T. TRAXLER

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A series of chloroacids, RR'CClCOOH (where R and/or R' = hydrogen, alkyl or phenyl) and their esters were reduced with lithium aluminum hydride in excess. The products were chlorohydrins, $RR'CClCH_2OH$, alcohols, $RR'CHCH_2OH$, aldehydes, RR'CHCHO and glycols, $RR'COHCH_2OH$ with the glycols being formed in substantial amounts only if at least one of the R-groups is phenyl. Preliminary evidence was obtained that the chlorohydrins are intermediate in the reduction of chloroacids to alcohols. The ease of reduction of the chlorine (as measured by the ratio: yield of alcohol/yield of chlorohydrin) is greater in either primary or tertiary chloroacids than in secondary, suggesting that two different mechanisms account for the removal of the halogen. Aldehydes are formed when R is phenyl and R' is phenyl or methyl; their origin was traced to the primary formation of an enolate salt. Chlorohydrins can be obtained from a number of chloroesters RR'CClCOOR" in good yield by the inverse addition of one-half mole of lithium aluminum hydride to one mole of ester.

The reduction of simple primary alkyl chlorides with lithium aluminum hydride in ether solution is usually ineffective, although the reduction can be performed quite readily in boiling tetrahydrofuran.[4] Thus *n*-butyl chloride is reported[5] not to be reduced in ether solution at 25° and in the present work it was found that the phenyl- and phenoxy-substituted halides shown in Table I were reduced only to the extent of 17% or less.

TABLE I

REDUCTION OF ALKYL CHLORIDES WITH LITHIUM ALUMINUM HYDRIDE IN BOILING ETHER[6]

Chloride	Reduction, %	Recovery, %
$PhCH_2CH_2Cl$	4	79
$PhCH_2CH_2CH_2Cl$	8	75
$PhOCH_2CH_2Cl$	2	89
$PhOCH_2CH_2CH_2Cl$	17	77
n-C_4H_9Cl	No redn. at 25°[5]	

Secondary and tertiary halides are reduced even more sluggishly,[4,7,8] as would be expected in view of the fact that the lithium aluminum hydride reduction of alkyl halides is a bimolecular nucleophilic displacement reaction.[7,9] In contrast, we have observed[1] that the tertiary chloride 2-phenyl-2-chloropropionic acid, $CH_3CCl(Ph)COOH$ (I) is reduced readily, the principal reduction product of I or its methyl ester being the chlorine-free alcohol 2-phenylpropanol, $CH_3CH(Ph)CH_2OH$. Fragmentary results of other investigators suggest that reduction of chlorine in reactions where chloroalcohols are the expected products is fairly general. Thus poor yields were reported in the reduction of chloroacetic acid and its ethyl ester to ethylene chlorohydrin (13 and 37%, respectively)[10] and of chloroacetone[11a] and bromoacetone[11b] to the corresponding 1-halo-2-propanols (44 and 48%, respectively). Low boiling fractions (probably having the chloride function reduced) were reported in the reduction of 4-chloro-2-butanone[12] and of ethyl (1-hydroxy - 2 - methyl) - cyclohexylchloroacetate.[13] Moreover, the reduction of epichlorohydrin gives the chlorine-free product propanol-2 in 88% yield.[7] In all these instances the "direct addition" technique was employed, yet chloroacid chlorides can be reduced to chlorohydrins in good yields even by the ordinary technique of adding the halide to a slight excess of ethereal lithium aluminum hydride. Thus chloroacetyl chloride is reduced to ethylene chlorohydrin in 62% yield[10] and the corresponding reduction of 2-chloropropionyl chloride gives the chloro-

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[1] Previous paper in this series: E. L. Eliel and J. P. Freeman, THIS JOURNAL, **74**, 923 (1952).

[2] Presented in part before the Organic Division of the American Chemical Society at Atlantic City, N. J., on September 17, 1952.

[3] This paper is taken in part from the Ph.D. dissertation of Sr. M. Carolyn, R.S.M.

[4] J. E. Johnson, R. H. Blizzard and H. W. Carhart, THIS JOURNAL, **70**, 3664 (1948).

[5] R. F. Nystrom and W. G. Brown, *ibid.*, **70**, 3738 (1948).

[6] The chlorides in this table as well as ethylene chlorohydrin are of about the same reactivity as *n*-butyl chloride in typical S_N2 reactions, such as the reaction with iodide ion in acetone: J. B. Conant and W. R. Kirner, *ibid.*, **46**, 232 (1924); W. R. Kirner, *ibid.*, **48**, 2745 (1926).

[7] L. W. Trevoy and W. G. Brown, *ibid.*, **71**, 1675 (1949).

[8] See also W. G. Brown in R. Adams, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. VI, p. 469 (1951).

[9] Exceptions are some highly fluorinated and phenylated halides: J. C. Tatlow and R. E. Worthington, *J. Chem. Soc.*, 1251 (1952); J. Roylance, J. C. Tatlow and R. E. Worthington, *ibid.*, 4426 (1954), and ref. 8, p. 481.

[10] C. E. Sroog, C. M. Chih, F. A. Short and H. M. Woodburn, THIS JOURNAL, **71**, 1710 (1949).

[11] (a) C. A. Stewart and C. A. VanderWerf, *ibid.*, **76**, 1259 (1954); (b) K. Kakemi, F. Kusuda and R. Morii, *J. Pharm. Soc. Japan*, **75**, 110 (1955).

[12] F. Sondheimer and R. B. Woodward, THIS JOURNAL, **75**, 5438 (1953).

[13] J. D. Billimoria, *J. Chem. Soc.*, 2626 (1953).