taining the aluminum bromide was placed in the neck of the flask, the flask evacuated through the side arm and the break tip on the ampule broken against the bottom of the stopper in the flask. The catalyst was transferred into the flask by gentle heating, dry nitrogen admitted through the side arm, and the empty ampule removed in a steady flow of the gas. The flask was again evacuated and the solvent drawn up into the flask through the side-arm. An approximate concentration could be calculated from the weight of the ampule before and after transfer of the catalyst. The exact concentration was determined by titration (see below). Samples were removed from the flask only in a stream of dry nitrogen to minimize the introduction of traces of moisture.

Procedure for Kinetic Determination.—The rates were measured using a "fragile bulb technique."[4] The reactants were added with a 1-cc. rapid delivery pipet at 25°. The reaction bulbs were immediately closed with a rubber cap slipped over the stem, then shaken and immersed in a constant temperature bath. It was necessary to wash and dry the pipet between each addition of the catalyst solution. The reaction time was measured from the start of addition of the catalyst solution. At the proper time, each bulb was removed from the bath, the outside washed off with distilled water, and then placed in a 250-ml. wide mouth erlenmeyer flask containing 30 cc. of cold distilled water. After stoppering the flask, the bulb was broken by shaking the flask, quenching the reaction.

The titration procedure was described previously.[4] The concentration of the catalyst was determined by titration of blanks which were carried through the same procedure as the reaction samples, but without having aromatic and alkyl bromide present. The amount of reaction was determined by titration from the difference between the hydrogen bromide present in the sample and that found in the blanks.

The pseudo-first order rate constants were determined graphically. Typical data are shown in Fig. 3. The values of k_3 were determined by dividing the graphical k_1 values by the concentrations of benzene and alkyl bromide.

Side Reactions.—The absence of any significant side reactions during methylation and ethylation of benzene and toluene was established by treating methyl and ethyl bromides with aluminum bromide in 1,2,4-trichlorobenzene at the temperatures and reaction times used in the alkylation studies. Failure to observe any significant change with time in the titer for the catalyst eliminated the possibility of a competitive alkylation of the solvent or of an elimination reaction of the alkyl bromide. An approximate rate constant for the formation of hydrogen bromide from ethyl bromide at 25°, $k_2 = 1.7 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$, shows it to be much smaller than the alkylation rate and unimportant in the kinetics.

Acknowledgment.—We wish to acknowledge the financial assistance provided by the Standard Oil Company (Indiana) in the form of two fellowship grants.

Lafayette, Indiana

[Contribution from the Department of Chemistry of Purdue University]

Steric Effects in Elimination Reactions. VI. The Effect of the Steric Requirements of the Alkyl Group on the Direction of Bimolecular Elimination

By Herbert C. Brown, Ichiro Moritani[1] and M. Nakagawa[1]

Received October 26, 1955

A series of related tertiary bromides, $RCH_2CBr(CH_3)_2$, has been dehydrobrominated by pyridine and by potassium ethoxide (1 *M* solution in ethanol). With increased branching of the group R (Me < Et < *i*-Pr < *t*-Bu) there is observed a regular increase in the ratio of 1-/2-olefin in the product. This transition from Saytzeff- to Hofmann-type elimination is attributed to the steric requirements of the alkyl group R. It is proposed that with the increasing steric requirements of the group R the transition state leading to the 2-olefin becomes less favored energetically than that leading to the 1-olefin.

Directive effects in elimination reactions have been discussed previously by Hughes, Ingold and their co-workers.[2] They pointed out for the first time the existence of two conflicting rules governing the direction of elimination. They proposed that all unimolecular eliminations as well as bimolecular eliminations of uncharged molecules should proceed to give the most branched olefin (Saytzeff rule), while bimolecular eliminations of 'onium salts should proceed to give the least branched olefin (Hofmann rule). They attributed the Saytzeff rule to control by the electromeric factor, and the Hofmann rule to control by the polar factor rendered important by the positive charge in the 'onium ion.

The observation that the solvolysis of dimethylneopentylcarbinyl chloride proceeds to give predominantly 2,4,4-trimethyl-1-pentene,[3] a case of Hofmann-type elimination in an unimolecular reaction, led us to question this interpretation. We therefore undertook an examination of the possible role of steric effects in controlling the direction of olefin formation in both unimolecular and bimolecular elimination. The role of steric effects in unimolecular elimination reactions has been discussed previously.[4] The importance of the steric factor in directing elimination in bimolecular reactions is the subject of the present group of papers.

Consideration of the possible role of steric effects in bimolecular elimination reactions suggested that the direction of elimination might be influenced by (a) the steric requirements of the alkyl groups on the incipient double bond, (b) the steric requirements of the attacking base, and (c) the steric requirements of the leaving group. The first of these factors was examined by studying the effects of the steric requirements of the group R in the series of tertiary bromides, $RCH_2CBr(CH_3)_2$, on the nature of the olefins formed in eliminations by potassium ethoxide and by pyridine. The results are reported in the present paper.

Results

The four tertiary bromides $RCH_2CBr(CH_3)_2$, with R = Me, Et, *i*-Pr and *t*-Bu, were dissolved in a

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[1] Post-doctorate assistants at Purdue University, 1951–1953 and 1953–1954, respectively, on a contract supported by the Office of Naval Research and a grant provided by the National Science Foundation.

[2] M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw and L. I. Woolf, *J. Chem. Soc.*, 2093 (1948).

[3] H. C. Brown and H. L. Berneis, This Journal, **75**, 10 (1953).

[4] (a) H. C. Brown and I. Moritani, *ibid.*, **77**, 3607 (1955); (b) H. C. Brown and M. Nakagawa, *ibid.*, **77**, 3610 (1955); (c) **77**, 3614 (1955); (d) H. C. Brown and Y. Okamoto, *ibid.*, **77**, 3619 (1955); (e) H. C. Brown and I. Moritani, *ibid.*, **77**, 3623 (1955).

small excess of 1.0 *M* potassium ethoxide in absolute ethanol.[5] After several hours at 70 ± 10°, the mixture was heated to its boiling point and the olefin recovered by fractionation through a Todd micro column. In the case of the less volatile olefins, the product was recovered by dilution of the reaction mixture with water.

The olefins were washed several times with cold water and dried over anhydrous magnesium sulfate. The recovery procedures were thoroughly tested on synthetic mixtures of the pure olefins. It was established that no isomerization of the olefins occurred under the conditions of the elimination reaction or of the isolation procedure.

Analysis was primarily by refractive index. In several instances the analytical results thus obtained were checked by infrared analysis. In all cases the results of the two methods agreed within the probable limits of error of the analysis (±3%).[6]

The results are summarized in Table I.

TABLE I

COMPOSITION OF OLEFINS FORMED IN THE DEHYDROHALOGENATION OF ALKYLDIMETHYLCARBINYL BROMIDES BY POTASSIUM ETHOXIDE[a]

t-Bromide, $RCH_2CBr(CH_3)_2$	R	Composition, % 1-Olefin	2-Olefin
t-Amyl bromide[c]	Me	30	70
2-Methyl-2-bromopentane	Et	50	50
2,4-Dimethyl-2-bromopentane	*i*-Pr	54	46
2,4,4-Trimethyl-2-bromopentane	*t*-Bu	86[b]	14[b]

[a] Potassium ethoxide, 1.0 *M*, except where otherwise noted. [b] Potassium ethoxide, 4.0 *M*. [c] M. L. Dhar, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2065 (1948), report 28% 1-olefin in dehydrohalogenation with sodium ethoxide at 25°.

Heterocyclic bases have been commonly applied for dehydrohalogenation reactions in synthetic chemistry. Although no mechanistic study of this reaction has been made, it appears reasonable that the reaction is a bimolecular elimination involving an attack by the heterocyclic base on the β-hydrogen atom. Accordingly, it appeared of interest to examine the nature of the olefins formed in the dehydrohalogenation of this series of tertiary bromides by pyridine.

In these experiments sufficient tertiary bromide was dissolved in pure pyridine so as to give a 1.0 *M* solution. The reaction mixture was heated to boiling and the olefin distilled out of the reaction mixture. The product was washed with water, dried and analyzed by refractive index. A number of blank experiments established that no isomerization of the olefin occurred under either the dehydrohalogenation or the isolation procedures.

TABLE II

COMPOSITION OF THE OLEFINS FORMED IN THE DEHYDROHALOGENATION OF ALKYLDIMETHYLCARBINYL BROMIDES BY PYRIDINE

t-Bromide, $RCH_2CBr(CH_3)_2$	R	Composition, % 1-Olefin	2-Olefin
t-Amyl bromide	Me	25	75
2-Methyl-2-bromopentane	Et	32	68
2,4-Dimethyl-2-bromopentane	*i*-Pr	44	56
2,4,4-Trimethyl-2-bromopentane	*t*-Bu	70	30

The experimental results are summarized in Table II.

Discussion

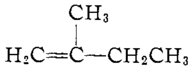
It is apparent that both with pyridine and with potassium ethoxide there is a regular increase in the ratio of 1-/2-olefin formed in the dehydrohalogenation reaction with increasing branching of the alkyl group R (Table III).

TABLE III

RATIO OF 1-/2-OLEFIN FORMED IN THE DEHYDROHALOGENATION OF ALKYLDIMETHYLCARBINYL BROMIDES

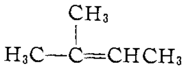
t-Bromide, $RCH_2CBr(CH_3)_2$	R	Ratio of 1-/2-olefin Pyridine	KOC_2H_5
t-Amyl bromide	Me	0.33	0.43
2-Methyl-2-bromopentane	Et	.47	1.00
2,4-Dimethyl-2-bromopentane	*i*-Pr	.81	1.17
2,4,4-Trimethyl-2-bromopentane	*t*-Bu	2.33	6.14

The preferential formation of the 2-olefin in the elimination reactions of *t*-amyl halides was attributed by Hughes, Ingold and their co-workers to hyperconjugative stabilization of the transition state.[2] That is to say, the transition state leading to the 2-olefin (2-methyl-2-butene) will have nine carbon–hydrogen bonds suitable for hyperconjugative interaction with the incipient double bond (II), whereas the 1-olefin (2-methyl-1-butene) will have only five carbon–hydrogen bonds capable of such interaction (I). This explanation appears quite reasonable.



$$\mathrm{H_2C{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_2CH_3}$$

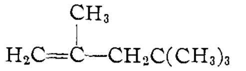
I



$$\mathrm{H_3C{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CHCH_3}$$

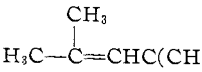
II

Successive replacement of the hydrogen atoms in one of the methyl groups by one, two and three methyl groups will, of course, reduce the possibilities for hyperconjugative interactions by the neighboring carbon–hydrogen bonds. Thus 2,4,4-trimethyl-2-pentene (IV) will have but six such hydrogen atoms as compared to five in 2,4,4-trimethyl-1-pentene (III).



$$\mathrm{H_2C{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_2C(CH_3)_3}$$

III



$$\mathrm{H_3C{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CHC(CH_3)_3}$$

IV

On this basis a slight increase in the 1-/2-olefin ratio might have been anticipated with increasing branching of the alkyl group R. However, a regular transition to predominant formation of the 1-olefin does not appear to be explicable in terms of such hyperconjugative interactions. This is especially true when it is recognized that carbon-to-carbon bonds possess hyperconjugative possibilities only slightly smaller than those of carbon-to-hydrogen bonds.

For example, in the solvolysis of *p*-alkylbenzhydryl chlorides, the relative rates observed are: H, 1.00; Me, 23.4; Et, 22.4; *i*-Pr, 20.0; *t*-Bu, 18.6.[7]

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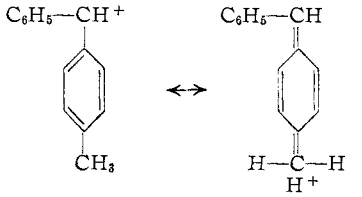
(5) In the following paper [H. C. Brown, I. Moritani and Y. Okamoto, THIS JOURNAL, **78**, 2193 (1956)] evidence is presented that under these conditions the formation of olefin arises predominantly from reaction of the ethoxide with the tertiary bromide with only a minor contribution from a solvolytic reaction.

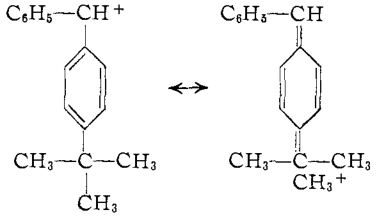
(6) See Table IV, ref. 4b, for typical results obtained in analyses of mixtures of 1- and 2-olefins by the two procedures.

(7) E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 949 (1940).

That is to say, the large increase observed for *p*-Me, primarily attributable to hyperconjugative stabilization of the carbonium ion V, is almost completely retained in the *t*-Bu derivative VI.



V



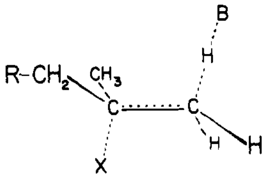
VI

Similarly, in the solvolysis of the substituted phenyldimethylcarbinyl chlorides we have observed the following relative rates (90% acetone, 25°): H, 1.00; *m*-Me, 2.00; *m*-*t*-Bu, 1.85; *p*-Me, 26.0; *p*-*t*-Bu, 14.4[8]. Here again the large effect of *t*-butyl in the *para* as compared to the *meta* position apparently requires a large hyperconjugative contribution from the *t*-butyl group.

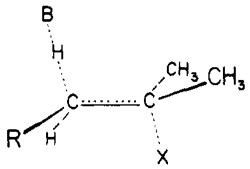
It appears therefore that the decreased possibilities for hyperconjugative stabilization of the transition state leading to the 2-olefin cannot account for the large increases in the 1-/2-olefin ratios observed with increasing branching of the groups R. It is possible to account for the marked shift in the ratio in terms of the steric requirements of the groups R in the transition state.

Considerable evidence has now been accumulated to favor the view that the preferred transition state for the bimolecular elimination reaction is one in which the four atoms involved in the reaction have a planar *trans* arrangement.[9]

On this basis the transition states for olefin formation for the tertiary bromide can be represented as (VII, VIII)



VII, transition state leading to 1-olefin



VIII, transition state leading to 2-olefin

As the steric requirements of R are increased there will be increasing steric interactions between the groups R and X in the transition state leading to the 2-olefin VIII, whereas the alternative transition state will not be seriously affected. Consequently, with increasing steric requirements of R there would be observed a decreasing tendency for the reaction to proceed to the formation of the 2-olefin and there should result an increase in the 1-/2-olefin ratio.

This interpretation leads to the conclusion that it should also be possible to modify the 1-/2-olefin ratio by increasing the steric requirements of the group X. On this basis the observation that 'onium salts undergo elimination to form predominantly the 1-olefin would be due not to the presence of the positive charge in the 'onium salt,[2] but due instead to the large steric requirements of the group undergoing elimination (X = $-\overset{+}{N}Me_3$, $-\overset{+}{S}Me_2$).[10] These possibilities are examined in the following papers.

Experimental Part

Materials.—The preparation and physical properties of the tertiary alcohols and bromides used in this study have been described previously.[4b]

Commercial absolute alcohol was refluxed with magnesium ethylate for six hours and then distilled through a column. Potassium was dissolved in this material with exclusion of air and moisture in preparing the potassium ethoxide solutions utilized for the eliminations.

The purest available grades of pyridine were heated under reflux for 3–4 hours over calcium hydride and then distilled from the calcium hydride through an efficient column (b.p. 113° (750 mm.), n^{20}D 1.5092).

Procedure for Elimination Experiments.—The *t*-alkyl bromide was mixed with base in a round-bottomed flask provided with a mercury well for the thermometer. In general, approximately 0.1 mole of the bromide was mixed with approximately 100 ml. of the base (1.0 *M* potassium ethoxide or pure pyridine). The mixture was maintained at 70 ± 10° for several hours. It was then attached to a Todd column and heated to reflux temperature. The olefin was collected at the top of the column along with small quantities of either ethanol or pyridine in the respective cases.

The distillate was washed with water several times and then dried over anhydrous magnesium sulfate. In the case of the low boiling olefins the receiver was cooled with an

TABLE IV

OLEFIN ANALYSIS BASED ON REFRACTIVE INDEX

	Synthetic olefin mixtures	Wt., %	n^{20}D	Anal.,[a] %
1.	2,3-Dimethyl-1-butene	42.4	1.4030	42.5
	2,3-Dimethyl-2-butene	57.6		57.5
2.	2,3-Dimethyl-1-butene	69.0	1.3969	70.0
	2,3-Dimethyl-2-butene	31.0		30.0
3.	2,4,4-Trimethyl-1-pentene	50.0	1.4122	51.0
	2,4,4-Trimethyl-2-pentene	50.0		49.0
4.	2,4,4-Trimethyl-1-pentene	38.5	1.4132	38.0
	2,4,4-Trimethyl-2-pentene	61.5		62.0
5.	2,4,4-Trimethyl-1-pentene	24.9	1.4141	24.3
	2,4,4-Trimethyl-2-pentene	75.1		75.7

[a] Based upon a linear interpolation of the refractive index values for the pure olefins.

TABLE V

COMPARISON OF ANALYSES OF OLEFIN PRODUCTS BY INFRARED AND REFRACTIVE INDEX

		Olefin analysis			
		n^{20}D		Infrared	
Halide	Base	1-	2-	1-	2-
t-Amyl bromide	2,6-Lutidine	45	55	43	57
t-Amyl bromide	2-Picoline	30	70	31	69
2,3-Dimethyl-2-bromobutane	2,6-Lutidine	42	58	44	(56)[a]
2,4,4-Trimethyl-2-bromopentane	Potassium *t*-butoxide	97	3	98	(2)[a]

[a] Analysis based upon the 1-component.

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(8) Unpublished work with J. D. Brady, M. Grayson and W. H. Bonner.

(9) W. Huckel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940); S. J. Cristol, THIS JOURNAL, **69**, 338 (1947); **71**, 1894 (1949); S. J. Cristol, N. L. Hause and J. S. Meek, *ibid.*, **73**, 674 (1951); D. H. R. Barton and E. Miller, *ibid.*, **72**, 1066 (1950).

(10) C. H. Schramm, *Science*, **112**, 367 (1950).

TABLE VI

SUMMARY OF EXPERIMENTAL DATA ON THE YIELD AND COMPOSITION OF OLEFINS FORMED IN THE DEHYDROHALOGENATION OF *t*-ALKYL BROMIDES WITH PYRIDINE AND POTASSIUM ETHOXIDE

Tertiary bromide, $RCH_2CBr(CH_3)_2$			Base, ml.	Olefin g.	Yield, %	Olefin $n^{20}D$	Composition	
	G.	Moles					1-%	2-%
t-Amyl bromide	15.10	0.10	100, 1.0 *M* EtOK	6.30	90	1.3847	29	71
	15.10	.10	100, 1.0 *M* EtOK	5.79	83	1.3846	28	72
	15.10	.10	100, 1.0 *M* EtOK	5.18	74	1.3843	32	68
	12.05	.08	80, pyridine	4.95	90	1 3850	25	75
	15 10	.10	100, pyridine	6.38	91	1.3850	25	75
2-Methyl-2-bromopentane	8.25	.05	50, 1.0 *M* EtOK	2.56	61	1.3958	51	49[a]
	12.00	.067	100, 1.0 *M* EtOK	4.68	84	1.3960	49	51
	16.50	.10	100, pyridine	7.50	88	1.3975	32	68
2,4-Dimethyl-2-bromopentane	8.95	.05	50, 1.0 *M* EtOK	3.04	63	1.4010	54	46[a]
	17.90	.10	100, pyridine	8.50	87	1.4015	44	56
2,4,4-Trimethyl-2-bromopentane	19.30	.10	100, 4.0 *M* EtOK	7.56	68	1.4096	86	14[a]
	19.30	.10	100, pyridine	9.43	84	1.4107	71	29
	19.30	.10	100, pyridine	10.45	93	1.4108	70	30

[a] The reaction mixture was poured into water, the olefin layer separated and distilled.

ice-bath and the washings were carried out at 0° by using an ice-water jacketed separatory funnel.

The isolation procedure was modified in the potassium ethoxide elimination reactions that produced olefins boiling near ethanol. The reaction mixture was poured into ice-water and the olefin fraction separated, washed with water and distilled, using pyridine or one of its higher homologs as a chaser. The olefin was again washed, thoroughly dried and analyzed. This procedure resulted in decreased yields of olefin, but no change in the isomer composition was observed.

Analysis was based primarily on refractive index measurements checked occasionally by infrared determinations. The refractive index values used for the individual components have been recorded previously.[4b]

It was established earlier that the refractive indices of mixtures of 1- and 2-amylenes fit a linear interpolation formula.[11] We established that the same holds for other olefins formed in the elimination reactions.

Typical results are summarized in Table IV.

The extent of the agreement realized in the infrared checks of the reaction products obtained in these studies is indicated by the data in Table V.

All elimination procedures were carefully checked with synthetic mixtures of pure olefins to ensure that neither isomerization nor fractionation of the olefins was a significant factor in the composition of the olefins isolated from the reaction mixtures.

The experimental results are summarized in Table VI.

Acknowledgment.—The studies reported in the present papers were greatly assisted by samples of the pure olefins from the American Petroleum Institute Project No. 45 at The Ohio State University and from the National Bureau of Standards. This assistance is gratefully acknowledged.

LAFAYETTE, INDIANA

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[11] M. L. Dhar, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2065 (1948).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Steric Effects in Elimination Reactions. VII. The Effect of the Steric Requirements of Alkoxide Bases on the Direction of Bimolecular Elimination

BY HERBERT C. BROWN, ICHIRO MORITANI[1] AND Y. OKAMOTO[2]

RECEIVED OCTOBER 26, 1955

The effect of the steric requirements of the attacking base on the direction of elimination has been studied by examining the products formed in treating representative secondary and tertiary bromides with the potassium salts of ethanol, *t*-butyl alcohol, *t*-amyl alcohol and triethylcarbinol in the respective alcohols as solvents. In the case of *t*-amyl bromide the percentage of 1-olefin in the product increases from 30 to 72, to 78, and finally to 89 for the four bases, respectively. Similar increases in the yield of the 1-olefin with increasing steric requirements of the alkoxide base were observed for 2-bromobutane, 2-bromopentane, 2,3-dimethyl-2-bromobutane and 2,4,4-trimethyl-2-bromopentane. Bimolecular rate data for the reaction of potassium *t*-butoxide with various alkyl bromides indicate that the increase in yield of the 1-olefin is primarily the result of a decrease in the rate of removal of the hydrogen in the hindered 3-position. It is therefore possible to shift elimination from essentially Saytzeff-type to essentially Hofmann-type by increasing the steric requirements of the attacking base.

According to the interpretation proposed in the previous paper,[3] it should be possible to exercise some measure of control over the direction of the bimolecular elimination reaction by modifying the steric requirements of the attacking base. In order to examine this possibility, a study was undertaken of the olefin distribution afforded by alkoxide bases of increasing steric requirements: $C_2H_5O^-$, $(CH_3)_3CO^-$, $C_2H_5(CH_3)_2CO^-$ and $(C_2H_5)_3CO^-$.[4] In the course of this study it also proved of interest to establish the rates of the bimolecular reaction of potassium *t*-butoxide with a number of secondary and tertiary alkyl bromides. With these data it becomes

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[1] Post-doctorate Assistant at Purdue University, 1951–1953, on a contract supported by the Office of Naval Research for the study of "Steric Strains in Chemical Reactions."

[2] Graduate Assistant at Purdue University, 1952–1955, on a contract supported by the Office of Naval Research for the study of "Steric Strains in Chemical Reactions."

[3] H. C. Brown, I. Moritani and M. Nakagawa, THIS JOURNAL, **78**, 2190 (1956).

[4] A preliminary communication of the results was published previously: H. C. Brown and I. Moritani, *ibid.*, **75**, 4112 (1953).