The data obtained for *cis*-2-methylcyclopropylmethylcarbinol were bp 81–83° (93 mm); ir (CCl$_4$) 3600, 3360 (OH), 1075, 1030, 1010, 995, 950, 910, 880, and 850 cm^{-1}; nmr (CCl$_4$) δ 3.83 (s, 1, OH), 3.28 (m, 1, CHOH), 1.23 (d, 3, J = 6 Hz, CH$_3$CHOH), 1.03 (d, 3, J = 3 Hz, c-C$_3$H$_5$CH$_3$), 0.87–0.75 (m, 3, cyclopropyl H), 0.1 (m, 1, cyclopropyl H); mass spectrum (prominent peaks) m/e 85 (M − 15), 82 (M − 18), 71, 67, 58 (B), 45.

Anal. Calcd for C$_6$H$_{12}$O (100.17): C, 71.94; H, 12.07. Found: C, 71.96; H, 12.30.

***trans*-2-Methylcyclopropylmethylcarbinol.**—Using the same procedure as described above, *trans*-cyclopropylcarbinol was prepared from *trans*-3-penten-2-ol.[17,19] The data obtained for *trans*-2-methylcyclopropylmethylcarbinol were ir (CCl$_4$) 3600, 3380 (OH), 1245, 1110, 1075, 1020, 995, 960, 937, 890, and 860 cm^{-1}; nmr (CCl$_4$) δ 3.29 (s, 1, OH), 3.1 (m, 1, CHOH), 1.17 and 1.04 (m, 6, at 1.17 a doublet of doublets, J = 6 and 1 Hz; at 1.04 a distorted doublet), 0.52 and 0.21 (2 m, 4, cyclopropyl H).

Irradiations were conducted in 125 ml (*c* 0.4–0.2%) solutions with an immersed Hanovia 450-W lamp, held in a water-cooled jacket and surrounded by a Corex filter (λ >280 mμ). The solutions were degassed with helium. The reactions were followed by vpc on a 5% XF-1150 cyanosilicone column (10 ft × 0.125 in., 60°, on a F & M 5750 gas chromatograph). After irradiation the solvent was carefully distilled from the product mixture and the products were collected from a 10 ft × 0.375 in. 20% XF-1150 cyanosilicone column on an Aerograph A-90-P gas chromatograph. Analyses were conducted by the Microanalytical Laboratory, University of California, Berkeley, Calif.

Registry No.—1, 2371-81-5; 2, 2863-92-5; *cis*-2-methylcyclopropylmethylcarbinol, 19293-89-1; *trans*-2-methylcyclopropylmethylcarbinol, 19293-90-4.

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[18] I. M. Heilbron, E. R. H. Jones, and R. A. Raphael, *J. Chem. Soc.*, 264 (1943).

[19] K. N. Campbell and L. T. Eby, *J. Amer. Chem. Soc.*, **63**, 2683 (1941).

Reactivity Studies in Free-Radical α Bromination of Cyclopropyl Compounds by N-Bromosuccinimide

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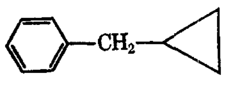
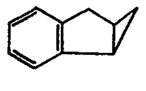
The relative reactivities of benzylcyclopropane, *trans*-1-benzyl-2-methylcyclopropane, cycloprop[2,3]indene, and bicyclo[4.1.0]hept-3-ene toward α-hydrogen abstraction in N-bromosuccinimide bromination have been determined. Rate accelerations resulting from electron release by the cyclopropyl substituents α to the incipient radical centers have been observed.

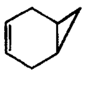
Product studies on the free-radical N-bromosuccinimide (NBS) brominations of the cyclopropyl compounds I, II, and III, which were reported earlier,[1]



I



II



III

showed that the reactions proceed predominantly *via* initial abstraction of hydrogen atoms from the carbons α to the cyclopropane rings. Bromide products resulting from both cyclopropylcarbinyl and rearranged allylcarbinyl radical intermediates were observed. No evidence was obtained, however, for the intermediacy of nonclassical cyclopropylcarbinyl radical species in product formation.

Various investigations[2] involving other methods for generation of cyclopropylcarbinyl radicals have also predominantly yielded either inconclusive or negative evidence for nonclassical intermediates in product formation. However, a number of examples have been reported[2e,3] in which α-cyclopropyl substituents do accelerate radical formation steps. Thus we became interested in determining whether rate acceleration also results from the presence of cyclopropyl substituents adjacent to the incipient radical centers in NBS α-bromination reactions. The model compounds, benzylcyclopropane (I), cycloprop[2,3]indene (II), and bicyclo[4.1.0]hept-3-ene (III), used for the reactivity investigation are the same as those used in the product study. Because of the difficulties involved in carrying out direct kinetic studies with heterogenous reactions, the alternate approach of investigating the relative rates of reaction of different substrates was used.

Results and Discussion

A summary of the reactivities relative to toluene toward NBS bromination at 77° in carbon tetrachloride solution for the compounds investigated is given in Table I. Literature values[4] for the relative reactivities in carbon tetrachloride solution of certain of the compounds and for several other compounds of interest are also given.

The data in Table I were obtained by successive comparisons of the relative reactivity values found for the individual competition experiments listed in Table II. Analyses of the competition product mixtures were done by quantitative nmr techniques[4a] as are described in the Experimental Section.

In most cases, hydrocarbon consumption and "normal bromide" formation per NBS reacted were approximately 90% or greater and no evidence was found in the nmr spectra of the competition product mixtures for significant side-product formation. Only in the competitions with benzylcyclopropane and *trans*-1-benzyl-2-

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[1] E. C. Friedrich, *J. Org. Chem.*, **34**, 528 (1969).

[2] (a) S. J. Cristol and R. V. Barbour, *J. Amer. Chem. Soc.*, **90**, 2832 (1968); (b) C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, **31**, 3381 (1966); (c) S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Amer. Chem. Soc.*, **80**, 635 (1958); (d) E. Renk, P. R. Shafer, W. H. Graham, R. H. Mazur, and J. D. Roberts, *ibid.*, **83**, 1987 (1961); (e) E. S. Huyser and J. D. Taliaferro, *J. Org. Chem.*, **28**, 3442 (1963).

[3] (a) C. G. Overberger and A. Lebovits, *J. Amer. Chem. Soc.*, **76**, 2722 (1954); (b) C. G. Overberger and M. B. Berenbaum, *ibid.*, **73**, 2618 (1951); (c) J. C Martin, J. E. Schultz, and J. W. Timberlake, *Tetrahedron Lett.*, **46**, 4629 (1967); (d) D. C. Neckers, A. P. Schaap, and J. Hardy, *J. Amer. Chem. Soc.*, **88**, 1265 (1966); (e) E. S. Huyser and D. T. Wang, *J. Org. Chem.*, **29**, 2720 (1964); (f) E. S. Huyser and L. R. Muson, *ibid.*, **30**, 1436 (1965); (g) C. Walling and P. S. Fredricks, *J. Amer. Chem. Soc.*, **84**, 3326 (1962).

[4] (a) S. S. Friedrich, E. C. Friedrich, L. J. Andrews, and R. M. Keefer, *J. Org. Chem.*, **34**, 900 (1969); (b) C. Walling, A. L. Rieger, and D. D. Tanner, *J. Amer. Chem. Soc.*, **85**, 3129 (1963); (c) M. M. Martin and G. J. Gleicher, *J. Org. Chem.*, **28**, 3266 (1963).

TABLE I

RELATIVE REACTIVITIES[a] OF VARIOUS COMPOUNDS TOWARD NBS BROMINATION

Compound	Relative Reactivities: Present work[b]	Relative Reactivities: Literature
Toluene (Std)	1.00	1.00
Isobutylbenzene	9.35 ± 0.31	
n-Butylbenzene	18.0 ± 0.46	28.5 ± 4[c]
Ethylbenzene		25.2 ± 0.46,[d] 23.6 ± 3.3[c]
Diphenylmethane		17.6 ± 0.3[d]
Benzylcyclopropane (I)	30.8 ± 0.88	
trans-1-Benzyl-2-methylcyclopropane	42.4 ± 0.74	
Allylbenzene	28.8 ± 0.58	26.2 ± 1.6[e]
Indan	92.8 ± 5.2	
Fluorene	32.8 ± 1.3	
Indene	76.0 ± 3.8	
Cycloprop[2,3]indene (II)	108 ± 5,[f] 119 ± 6[g,h]	
Cyclohexene	152 ± 7	129 ± 22[c]
Bicyclo[4.1.0]hept-3-ene (III)	260 ± 21	

[a] Per benzylic or allylic hydrogen. [b] At 77° in CCl_4 using azobisisobutyronitrile (AIBN) initiator. [c] Reference 4b, at 80° in CCl_4 using AIBN initiator. [d] Reference 4a, at 77° in CCl_4 using benzoyl peroxide initiator. [e] Reference 4c, at 69.50° in CCl_4 using photoinitiation. [f] From competition with cyclohexene. [g] From competition with fluorene. [h] Less accurate because of experimental difficulties.

TABLE II

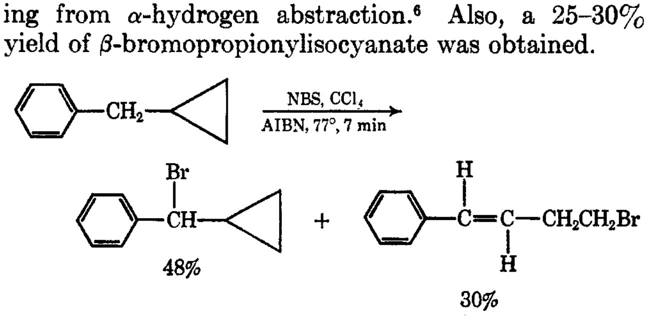
SUMMARY OF COMPETITIVE NBS BROMINATIONS[a]

A	B	k_a/k_b[b]	No. of runs
n-Butylbenzene	Diphenylmethane	1.02 ± 0.02	2[c]
Allylbenzene	Cumene	0.50 ± 0.005	2[c]
Isobutylbenzene	Diphenylmethane	0.53 ± 0.015	2[c]
Benzylcyclopropane	Diphenylmethane	1.75 ± 0.04	2[c]
trans-1-Benzyl-2-methylcyclopropane	Diphenylmethane	2.41 ± 0.01	2[c]
Fluorene	Cumene	0.57 ± 0.020	3[c]
Cyclohexene	Fluorene	4.65 ± 0.11	3[d]
Indan	Fluorene	2.83 ± 0.11	2[d]
Indene	Cyclohexene	0.50 ± 0.010	2[d]
Cycloprop[2,3]indene	Cyclohexene	0.71 ± 0.002	2[e]
Cycloprop[2,3]indene	Fluorene	3.62 ± 0.11	2[c,f]
Bicyclo[4.1.0]hept-3-ene	Cyclohexene	1.71 ± 0.11	3[e]

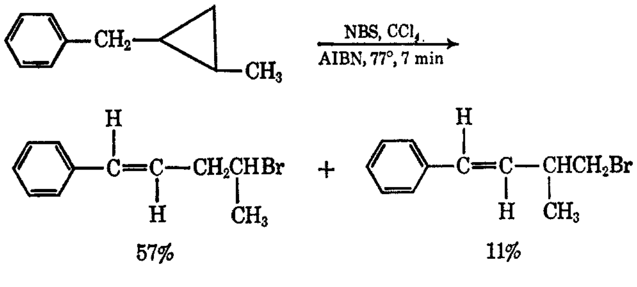
[a] At 77° in CCl_4 using AIBN initiator. [b] Per allylic or benzylic hydrogen. [c] Internal standard is benzyl chloride. [d] Internal standard is cumene. [e] Internal standard is diphenylmethane. [f] Less accurate because of experimental difficulties.

methylcyclopropane were low values obtained for substrate conversion.

For the benzylcyclopropane–diphenylmethane competitions, a 78% substrate conversion based on starting NBS was observed. This low substrate conversion must result mainly because of the observed formation of approximately a 10% yield of β-bromopropionylisocyanate from NBS rearrangement.[4b,5] In the earlier product study[1] it was observed that reaction of benzylcyclopropane with NBS in a 1:1 mol ratio gave only a 53% conversion of the benzylcyclopropane, and approximately 20% of the reacted benzylcyclopropane could not be accounted for as bromide products resulting from α-hydrogen abstraction.[6] Also, a 25–30% yield of β-bromopropionylisocyanate was obtained.



A similar argument holds for the *trans*-1-benzyl-2-methylcyclopropane–diphenylmethane competitions which showed only *ca.* 68% substrate conversions but from which approximately a 12% yield of β-bromopropionylisocyanate was observed. In the product studies,[1] reaction of *trans*-1-benzyl-2-methylcyclopropane with NBS in a 1:1 mol ratio resulted in 54% conversion of the starting material and gave a 68% yield of isomeric



allylcarbinylbromides *via* α-hydrogen abstraction. Ap-

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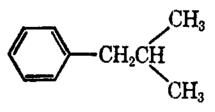
(5) (a) J. C. Martin and P. D. Bartlett, *J. Amer. Chem. Soc.*, **79**, 2533 (1957). (b) H. W. Johnson and D. E. Bublitz, *ibid.*, **79**, 753 (1957); **80**, 3150 (1958).

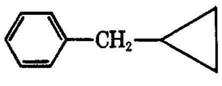
(6) The *ca.* 20% yield of undetermined, higher brominated materials observed in the product study may be accounted for as resulting from radical addition of bromine to the *trans*-1-phenyl-4-bromo-1-butene product rather than by addition of bromine to benzylcyclopropane. The former process gives a stabilized benzylic radical intermediate and should be favored over the latter which gives a secondary radical intermediate. Thus, the relative rate value of 30.8 for benzylcyclopropane given in Table I is felt to be that for α-hydrogen abstraction and not for competing processes.

proximately 22–25% of the NBS rearranged to β-bromopropionylisocyanate.

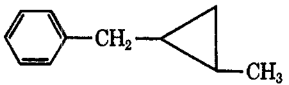
From the data in Table I it is apparent that rate acceleration of α-hydrogen abstraction in NBS bromination is definitely obtained with benzylcyclopropane (I). This material is as reactive as allylbenzene, is almost twice as reactive as diphenylmethane or *n*-butylbenzene, and is over three times as reactive as isobutylbenzene. The latter comparison is probably the best, from consideration of electronic stabilization and steric factors, for estimation of the magnitude of the cyclopropyl-induced acceleration. Evidence that the acceleration is due to an electron-releasing resonance effect by the cyclopropane ring is given by the observation that attachment of an electron-releasing *trans*-2-methyl substituent on benzylcyclopropane provides additional rate acceleration.[7]



k/k_{Tol} 9.35



k/k_{Tol} 30.8



k/k_{Tol} 42.4

Estimates of the magnitudes of the cyclopropyl accelerations in the cycloprop[2,3]indene (II) and bicyclo[4.1.0]hept-3-ene (III) systems could not be obtained in a straightforward manner. This is because of the difficulties involved in finding compounds to use as suitable bases for rate comparisons.

Compounds investigated as possible models for comparison with cycloprop[2,3]indene are indan, indene, and fluorene. However, both indene and fluorene are less reactive than indan. This must be related to a lowering of the ground-state free energies of fluorene and indene by resonance which is not compensated for by a corresponding lowering of the transition-state energies for hydrogen abstraction. Cycloprop[2,3]indene is, however, slightly more reactive than indan, and it is anticipated that a better compound for comparison, 2-methylindan, should be even less reactive than indan toward 1-hydrogen abstraction (*cf.* the relative rate values of *n*-butylbenzene and isobutylbenzene).

Only a single possible rate comparison, with cyclohexene, is available for bicyclo[4.1.0]hept-3-ene (III).[8] This cyclopropyl compound is of special interest since it is the only example investigated in which formation of a vinylcyclopropyl radical is involved. The fact that it is significantly more reactive than cyclohexene does indicate that the cyclopropyl substituent is providing some rate acceleration for α-hydrogen abstraction.

In conclusion, evidence was found with all of the cyclopropyl systems investigated for rate accelerations of hydrogen atom abstraction produced by the cyclopropyl substituents α to the incipient radical centers. The magnitudes of the accelerations are not large, but are well outside of experimental error. Evidence that the accelerations are probably due to electron release by the cyclopropyl substituents and not simply to release of strain at the transition states for hydrogen-atom abstraction was provided by the earlier product study.[1] The major products from the NBS α brominations of benzylcyclopropane (I) and cycloprop[2,3]indene (II) were found to possess retained cyclopropyl structures. However, it should be noted that only rearranged, allylcarbinyl products were observed from NBS bromination of bicyclo[4.1.0]hept-3-ene (III) and *trans*-1-benzyl-2-methylcyclopropane.

The mechanism of electron release by the cyclopropyl group in radical stabilization is still not clear. However, since evidence is available[9] which indicates that the cyclopropyl group should exhibit a rate-retarding polar inductive effect, the accelerations must be due to some type of electron release by resonance from the cyclopropane ring which stabilizes the activated complexes at the transition states for the radical formation steps. It is anticipated that future investigations of the reactivities of various mono- and dimethyl-substituted benzylcyclopropanes toward α-hydrogen abstraction may provide valuable information regarding the detailed nature of the electron-releasing resonance effect.

Experimental Section

Materials.—The methods of preparation and properties of benzylcyclopropane, *trans*-1-benzyl-2-methylcyclopropane, cycloprop[2,3]indene, and bicyclo[4.1.0]hept-3-ene are described elsewhere.[1] Commercial samples of *n*-butylbenzene, cumene, isobutylbenzene, fluorene, azobisisobutyronitrile (Eastman White Label), diphenylmethane, indan (Aldrich), benzyl chloride, cyclohexene (Mallinckrodt, AR), allylbenzene, 1,4-dihydrobenzene (Chemical Samples Co.), N-bromosuccinimide (Arapahoe), and carbon tetrachloride (J. T. Baker, AR) were used without further purification. Indene (Eastman Yellow Label) was purified before use by careful fractional distillation.

Competitive Brominations.—The choice of a particular pair of compounds used in an individual competition experiment was based both on the requirement that the compounds have similar reactivities toward NBS and the necessity that at least one-proton absorption for each of the compounds or their bromination products is resolved sufficiently for accurate quantitative measurements from all other proton absorptions in the nmr spectrum of the product mixture. In a typical experiment, 7 to 15 mmol of each of the competitors was weighed (using hypodermic syringes for liquids) into a 50-ml flask containing an 8–10 mmol weighed quantity of NBS covered with approximately 20–25 ml of carbon tetrachloride solvent. The exact ratios used of the two competing compounds and NBS depended on the relative reactivities of the competitors. When possible, ratios were varied in duplicate runs. The mixture was then treated with 0.1 g of azobisisobutyronitrile and heated quickly to reflux (reacting mixture 77°) while stirring with a magnetic stirrer. The apparatus was protected from atmospheric moisture by a drying tube filled with Drierite. When the reaction was completed (from 15 to 30 min following the induction period depending on the particular experiment), as indicated by the disappearance of NBS from the bottom of the reaction flask, refluxing was stopped and the mixture was cooled. An internal standard (*ca.* 4 to 6 mmol) was then weighed into the reaction mixture before sampling of the liquid portion for quantitative nmr analysis. The choice of internal standard was based on its suitability for the nmr analysis procedure, specifically on the chemical shift values of its proton absorptions.

Nmr Analyses.—Analyses of the NBS bromination competition mixtures were carried out in thin walled tubes using a Varian Associates Model A-60A instrument. Tetramethylsilane (TMS)

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[7] P. von R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 232 (1966).

[8] Attempts to obtain a reliable rate value for 1,4-cyclohexadiene which could be used for a second comparison were not successful. Formation of significant quantities of presumably dibrominated side products along with the normal product, benzene, were observed in competitions with this material: J. P. Wibaut and F. A. Haak, *Rec. Trav. Chim.*, **69**, 1387 (1950).

[9] (a) T. L. Brown, *J. Amer. Chem. Soc.*, **80**, 6489 (1958); (b) H. C. Brown and J. D. Cleveland, *ibid.*, **88**, 2051 (1966).

was employed as the standard for determining chemical shift values of individual proton absorptions. At least six integrations were carried out on selected proton absorptions for the competitors or their bromination products (or both) and the weighed internal standard. Integral amplitudes were maximized to obtain the highest possible accuracy. The average deviation of individual integrations from the mean was generally on the order of 1%. The average value from integration of each different proton absorption was then corrected for the number of protons contributing to the absorption. From these values, by comparison with the per hydrogen integration value obtained for the known amount of internal standard, it was possible to calculate the numbers of millimoles of each competitor which remained. In certain cases this could be done directly, and in the other cases it was done indirectly by substraction of the number of millimoles of a bromide product observed from the number of millimoles of competitor weighed into the reaction. A decision as to which one of these procedures or both were used depended on whether the individual proton absorptions necessary for nmr analysis were better separated for the starting materials or for their bromide products from other proton absorptions in the competition product mixtures. The average chemical shift values (δ in parts per million downfield from TMS), which vary slightly in different mixtures, for the various individual proton absorptions of the internal standards, competitors, and bromide products used for calculation of the product compositions are as follows: benzyl chloride, δ 4.5 (s, 2 H, CH$_2$Cl); diphenylmethane, 3.9 (s, 2 H, CH$_2$); benzhydryl bromide, 6.2 (s, 1 H, CHBr); cumene, 1.2 (d, 6 H, J = 6.5 Hz, CH$_3$); cumyl bromide, 2.1 (s, 6 H, CH$_3$); *n*-butylbenzene, 2.6 (t, 2 H, J = 7.5 Hz, C$_6$H$_5$CH$_2$); α-bromo-*n*-butylbenzene, 4.9 (t, 1 H, J = 7.5 Hz, C$_6$H$_5$CHBr); isobutylbenzene, 0.9 (d. 6 H, J = 6.5 Hz, CH$_3$), 2.5 (d, 2 H, J = 7.0 Hz, CH$_2$); α-bromoisobutylbenzene, 0.85 and 1.15 (for each, d, 3 H, J = 6.5 Hz, CH$_3$), 4.6 (d, 1 H, J = 8.0 Hz, CHBr); benzylcyclopropane, 0.2 (m, 2 H, cyclopropyl); *trans*-1-benzyl-2-methylcyclopropane, 0.4 (m, 4 H, cyclopropyl); fluorene 3.7 (s, 2 H, CH$_2$); 9-bromofluorene, 5.7 (s, 1 H, CHBr); 1-bromoindan, 5.3 (t, 1 H, J = 4.0 Hz, CHBr); indene, 3.3 (s, 2 H, CH$_2$), 6.3 (m, 1 H, CH$_2$CH=); cycloprop[2,3]indene, 0.0 (m, 1 H, cyclopropyl), 3.0 (m, 2 H, C$_6$H$_5$CH$_2$); 3-bromocyclohexene, 4.6 (m, 1 H, CHBr), 5.6 (m, 2 H, vinyl); and bicyclo[4.1.0]hept-3-ene, 0.3 (m, 2 H, cyclopropyl).

Calculation of Relative Reactivities.—Relative reactivities from individual competition experiments were calculated using the integrated rate equation (1), where A$_0$ and B$_0$ are the initial and A$_f$ and B$_f$ the final amounts of the two competitors. A

$$k_A/k_B = \log (A_0/A_f)/\log (B_0/B_f) \tag{1}$$

summary of the results obtained from the individual competitions, along with the number of runs carried out and the internal standard used in each competition, is given in Table II. Experimental errors are average deviations from the mean. The reactivities per active benzylic or allylic hydrogen relative to toluene given in Table I were obtained by stepwise comparisons of suitable pairs using the values of Friedrich, *et al.*,[4a] for the relative reactivities of diphenylmethane to toluene (17.6 ± 0.3) and cumene to toluene (57.5 ± 1.0). The indirect comparisons were necessary for purposes of accuracy because of the marked differences in reactivity between toluene and most of the compounds investigated. Experimental errors given in Table I were obtained by use of the usual formula[10] for propagation of errors.

Registry No.—I, 1667-00-1; II, 15677-15-3; III, 16554-83-9; NBS, 128-08-5; *trans*-1-benzyl-2-methylcyclopropane, 18933-49-8.

Acknowledgment.—The author is indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and to his wife, Sevgi Sümer Friedrich, for running a number of the nmr spectra.

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(10) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," 2nd ed, D. Van Nostrand and Co., Inc., New York, N. Y., 1956, p 515.

The Effect of Ring Size on the Rate of Reaction of Cycloalkyl Phenyl Ketones with Sodium Borohydride

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Kinetic experiments have been carried out for the reactions of acetophenone, cyclopropyl phenyl ketone, cyclobutyl phenyl ketone, cyclopentyl phenyl ketone, and cyclohexyl phenyl ketone with sodium borohydride at 0, 25 and 35°, respectively. At 0° the relative rates of the four cycloalkyl phenyl ketones are cyclopropyl, 0.12; cyclobutyl, 0.23; cyclopentyl, 0.36; and cyclohexyl, 0.25 (relative rate constant of acetophenone is unity). The data are discussed in terms of the conformation theory.

In the study of the effect of ring size on the rate of pyrolysis of cycloalkyl phenyl sulfoxides, Kice and Campbell[1] found that the relative rates of decomposition are in the following order: cyclopentyl > cyclohexyl < cycloheptyl. The pyrolysis rate seems to be related to the physical properties of the rings. The well-known heat of combustion per methylene group is in the same order. Measurements of diffusion coefficients of medium sized monocyclic compounds in carbon tetrachloride were also shown to follow this order.[2]

In this paper we report the results of a study on the effect of different ring sizes on the reactivity of some aromatic ketones. Brown and coworkers[3] have demonstrated that sodium borohydride is an excellent reagent to study kinetically the effects of structures on the reactivity of aldehydes and ketones. They have investigated[4-6] the reaction rates of sodium borohydride with various ketones including cyclic and bicyclic ketones, as well as aromatic and aliphatic ketones.

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(1) J. L. Kice and J. D. Campbell, *J. Org. Chem.*, **32**, 1631 (1967).

(2) S. F. Sun, R. J. Beshinske, and K. E. Van Holde, *J. Amer. Chem. Soc.*, **89**, 6417 (1967).

(3) H. C. Brown, E. J. Mead, and B. C. S. Rao, *ibid.*, **77**, 6209 (1955).

(4) (a) H. C. Brown, O. H. Wheeler, and K. Ichikawa, *Tetrahedron*, **1**, 214 (1957); (b) H. C. Brown and K. Ichikawa, *ibid.*, **1**, 221 (1957).

(5) H. C. Brown and K. Ichikawa, *J. Amer. Chem. Soc.*, **84**, 373 (1962).

(6) H. C. Brown and J. Muzzio, *ibid.*, **88**, 2811 (1966).