white powder. Analysis of this powder indicated the presence of up to 1.5% K_2CO_3 as an impurity. Samples that were below this 98.5% purity level were rejected. Dimethyl sulfoxide was dried and distilled over Linde 13X molecular sieves. Infrared, gas chromatographic and mass spectrometric techniques showed the presence of only one compound. The olefins used, 2-methyl-1-pentene, 2-methyl-2-pentene, 4-methyl-1-pentene and *cis*- and *trans*-4-methyl-2-pentene, were all API samples and contained at the most 0.5% impurity. The hydrocarbons were analyzed on a model #154 Perkin-Elmer gas chromatograph equipped with a 21-ft. column containing 3% squalane on firebrick. Operating conditions amenable for complete separations were attained at 25° with 10 p.s.i.g. of helium pressure.

All solutions of potassium *tert*-butoxide in dimethyl sulfoxide were prepared in a nitrogen-blanketed dry-box. Maximum water content was 10 parts per million as detected by a moisture conductivity cell. Solutions were prepared to give a desired molarity and then placed in the appropriate flask or vial fitted with an air-tight rubber cap. The vial was then set in a constant temperature bath (±0.5°). Usually no more than 5–10 cc. of dimethyl sulfoxide was used. Prethermostated olefin was then injected into this base solution by means of a glass syringe after complete temperature equilibration. If a nonstirred vial was used, the olefin–dimethyl sulfoxide base solution was shaken for a few seconds by hand and set back into the constant temperature bath. Samples were obtained by inserting a hypodermic syringe through the self-sealing neoprene diaphragm. These samples were either directly injected into the gas chromatograph or else 0.5-cc. samples were quenched by injection into 5 cc. of ice-water. In the latter case, a small amount of n-pentane (0.2–0.5 cc.) was added to the solution and the mixture shaken. The miscible water–dimethyl sulfoxide layer was frozen out on Dry Ice. A sample of supernatant pentane extract was then analyzed on the gas chromatograph. Analysis by both methods gave similar results. In certain experiments an inert hydrocarbon was added along with the olefin to the solvent–base system as an internal standard to determine whether the olefin was reacting to form materials other than the isomers in question.

Dielectric constants were measured at 25 ± 0.5° using a Sargeant oscillometer, model V.

[Contribution from the Esso Research and Engineering Co., Linden, N. J.]

Anionic Activation of C–H Bonds in Olefins. IV. Effect of Ring Size on Rate of Formation of Anions from Alkylidenecycloalkanes and Cycloalkanones

By A. Schriesheim, René J. Muller and C. A. Rowe, Jr.

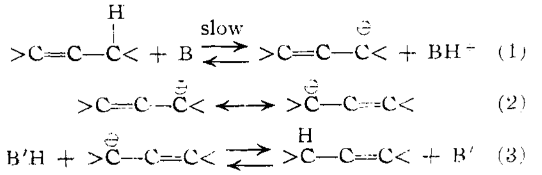
Received January 9, 1962

The isomerization of cyclic olefins in which the starting double bond is exocyclic to the ring has been studied. A homogeneous catalyst system, potassium *tert*-butoxide–dimethyl sulfoxide was used and the rate constants, activation energies and entropies were obtained. It was found that the isomerization rates were a function of ring size and the following order of reactivities holds at 55°: C_4-ring, 1070; C_5-ring, 454; C_6-ring, 1; C_7-ring, 5.8; C_8-ring, 17. A linear free-energy relationship was obtained between the isomerization rates and the rates for the base-catalyzed bromination of structurally similar ketones. The results are interpretable on the basis of a rate-determining step involving the removal of a proton followed by p-π-bond rehybridization to form an allylic anionic system. Stereoelectronic factors are postulated to play a key role in establishing such a system.

Since Freund[1] synthesized cyclopropane in 1882, a considerable amount of research effort has been expended on elucidating the chemistry of small-, common-, medium- and large-membered rings.[2] The reactivities of these cyclic compounds exhibit peculiarities which have been accounted for by several theories. For example, in a study of the reactivity of cyclic compounds. Brown introduced the now well-known concept of I-strain (from "internal"). The I-strain theory has been tested by Brown and others and has been somewhat modified.[3–8] Certain aspects have been criticized but, on the whole, I-strain provides a correlation for a vast amount of data. These correlations have been recently reviewed,[9] and Table I summarizes the effects of ring size on reaction rate for a number of mechanistically different reactions.

Several cases are known which do not follow the above predictions,[9] and Roberts[10–12] has presented data showing that electrical effects in small rings may be important.

Recently, strongly basic systems have been developed which are capable of activating C—H bonds in olefins at moderate temperatures.[13a,b,c] The system used in these studies was the base solvent combination potassium *tert*-butoxide–dimethyl sulfoxide. The postulated intermediates are allylic carbanions and the rate-determining step in the double bond isomerization is thought to be the abstraction of an allylic hydrogen by base.



$$>C{=}C{-}\overset{H}{\overset{|}{C}}< + B \underset{}{\overset{\text{slow}}{\rightleftarrows}} >C{=}C{-}\overset{\ominus}{C}< + BH^{+} \quad (1)$$

$$>C{=}C{-}\overset{\ominus}{\ddot{C}}< \longleftrightarrow >\overset{\ominus}{\ddot{C}}{-}C{=}C< \quad (2)$$

$$B'H + >\overset{\ominus}{\ddot{C}}{-}C{=}C< \rightleftarrows >\overset{H}{C}{-}C{=}C< + B' \quad (3)$$

There has not been any work reported on the rates of base-catalyzed movement of the *exo* to the

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[1] A. Freund, *Monatsh.*, **3**, 625 (1882).

[2] Terminology is that of H. C. Brown, R. S. Fletcher and R. B. Johannesen, *J. Am. Chem. Soc.*, **73**, 212 (1951).

[3] H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

[4] H. C. Brown, J. H. Brewster and H. Shechter, *ibid.*, **76**, 467 (1954).

[5] B. R. Fleck, *J. Org. Chem.*, **22**, 439 (1957).

[6] H. C. Brown, *ibid.*, **22**, 439 (1957).

[7] A. C. Cope, D. Ambrose, E. Ciganek, C. F. Howell and Z. Sacura, *J. Am. Chem. Soc.*, **81**, 3153 (1959); **82**, 1750 (1960).

[8] R. B. Turner and R. H. Gorner, *ibid.*, **80**, 1424 (1958); **79**, 253 (1957).

[9] For references, see the extensive review on "Strain and Reactivity in Monocyclic Systems," by Ya. I. Goldfarb and L. I. Belenkii, *Russian Chem. Rev.*, (*Uspekhi Khimii*), **29**, No. 4, pp. 214–235 (1960).

[10] J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5030 (1951).

[11] J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).

[12] J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951).

[13] (a) A. Schriesheim, J. E. Hofmann and C. A. Rowe, Jr., *ibid.*, **83**, 3731 (1961). (b) A. Schriesheim and C. A. Rowe, Jr., *ibid.*, **84**, (1962). (c) A. Schriesheim and C. A. Rowe, Jr., *Tetrahedron Letters*, in press (1962).

TABLE I

EFFECT OF RING SIZE AND MECHANISM ON REACTION RATE

Type of reaction	Small		Common			Medium	Large
	3-	4-	5-	6-	7-	8 to 12	13-
SN1, SN2 and free radical	Very slow	Slow	Fast	Slow	Fast	Fast	Medium
Addition to carbonyl group	Very fast	Fast	Slow	Fast	Slow	Slow	Medium

TABLE II

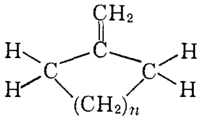
RATE CONSTANTS AND ACTIVATION PARAMETERS FOR ALKYLIDENECYCLOALKANE ISOMERIZATIONS

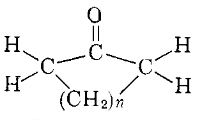
Ring size	4			5			6			7			8		
Temp., °C.	25	40	55	25	40	55	55	70	85	40	55	70	40	55	70
Rate constant,[a]															
k_1, sec.$^{-1}$ × 10^6	1067	4323	9171	245	947	3898	8.6	50.3	308	14.1	50.1	247	33.9	146	390
$\Delta H^{\ddagger}$, kcal./mole		13.3			17.3			27.1			19.7			16.8	
$\Delta S^{\ddagger}$, e.u.		−27.3			−17.0			0.7			−18.0			−25.4	
E_a, kcal./mole[b]		13.9			17.9			27.8			20.3			17.4	

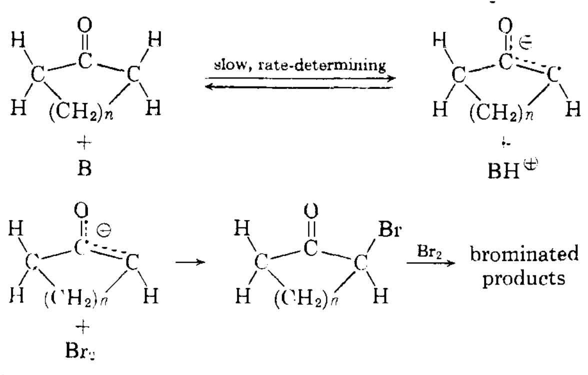
[a] Calculated from $k = 2.3 \log C_i - C_{eq.}/C_f - C_{eq.}/(t_2 - t_1)$ in 0.744 molar base and 1.22 molar olefin. [b] $E_a = \Delta H^* + RT$.

endo double bond in the alkylidene-cycloalkane series (methylenecyclobutane, etc.). The acid-catalyzed migration was studied by Cope, but only equilibrium positions were determined.[14] Rates of base-catalyzed migrations would provide fundamental knowledge concerning the factors influencing the activity of C–H bonds in olefins and, in addition, would help elucidate the chemistry of these cyclic compounds.

It is helpful to compare the relative rates of double bond migration in the *exo*-olefins (I) with a second reaction series in which the double bond moves into the ring and where the rate-determining step also involves the anionic activation of α-hydrogen atoms. For this comparison, a series of base-catalyzed brominations was carried out on the cycloalkanones II. It is well established that such base-catalyzed brominations involve formation of the enolate ion[15] as the rate-determining step. This reaction has been studied in detail by several investigators with a variety of ketones,[16–19] although the cycloalkanone series presently under study seems to have been overlooked except by Gerow.[20] The latter investigator studied the acid-catalyzed halogenation of the cycloalkanones (C_4 to C_8); however, this study was concerned with equilibrium keto-enol contents and not with rates.


I, n = 1 to 5


II, n = 1 to 5



Our study anticipated that a correlation between bromination and isomerization rates would serve as a basis for a discussion of the energy profile for these base-catalyzed reactions. The data shows that such a correlation does exist, and suggests that the controlling factors in the ketone enolization and the isomerization in the alkylidenecycloalkanes are stereoelectronic relationships governing the ease of allylic bond rehybridization.

Results

The base-catalyzed isomerization of the *exo* to the *endo* compound employing potassium *tert*-butoxide–dimethyl sulfoxide is first order in the alkylidenecycloalkanes in question. In all cases, rate data are based on less than 20% conversion.

The question of equilibrium composition is interesting and has been investigated by Cope[7] using an acid catalyst. The present investigation. however, was not concerned with equilibrium composition. Qualitatively, our results showed the *endo* isomer to be the more stable, and in all cases were in agreement with both Cope[7] and Turner.[8]

Table II shows the results of the isomerization for each cycloalkane derivative at three temperatures. Listed are the rate constants, activation energies (E_a) and also $\Delta H^{\ddagger}$ and ($\Delta S^{\ddagger}$).

Rate measurements were conducted at a single temperature for each olefin (55°). The values of the rate constant and the relative rates at this temperature are listed in Table III.

TABLE III

RATE CONSTANTS AND RELATIVE RATES FOR ALKYLIDENECYCLOALKANE ISOMERIZATIONS

Compound	Rate, sec.$^{-1}$ × 10^6	Rel. rate (C_6 = 1)
C_4	9171	1070
C_5	3898	454
C_6	8.6	1
C_7	50.1	5.8
C_8	146.4	17

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[14] A. C. Cope, *et al.*, *J. Am. Chem. Soc.*, **82**, 1750 (1960).

[15] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VIII.

[16] P. D. Bartlett, *J. Am. Chem. Soc.*, **56**, 967 (1934).

[17] R. P. Bell, R. D. Smith and C. A. Woodward, *Proc. Roy. Soc.* (*London*), **192**, 479 (1947).

[18] R. P. Bell, E. Gelles and E. Moller, *ibid.*, **198**, 308 (1949).

[19] R. P. Bell and O. M. Lidwell, *ibid.*, **176**, 88 (1940).

[20] A. Gerow, *J. Org. Chem.*, **26**, 3156 (1961).

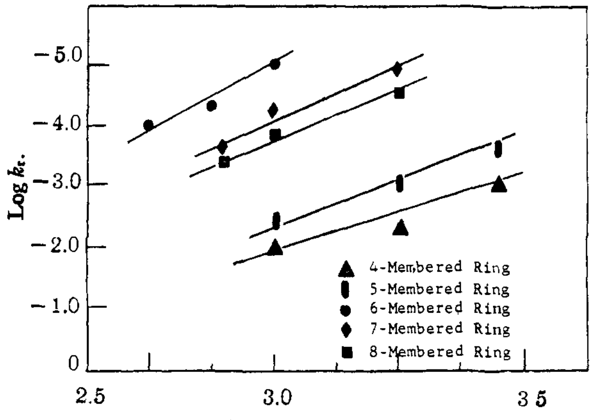
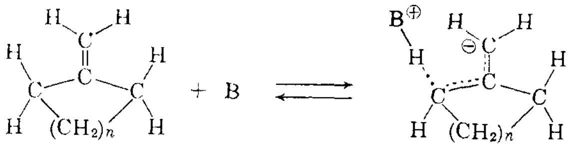


Fig. 1.—Temperature coefficient of base-catalyzed reaction rate for the isomerization of exocyclic olefins; log rate constant (k) *vs.* $1/T$.

These results show a rather striking effect of ring size on isomerization rate, with the smaller rings being by far the most reactive. The isomerization rate for the six-membered ring is the slowest of the series with that of the four-membered ring being 1070 times as fast and the five-membered ring being 454 times as fast. As ring size increases above C_6^-, the rates again increase and the seven-membered ring is about 5.8 times faster than the cyclohexane derivative while methylenecycloöctane is 17 times faster.

As with the straight-chained olefins (equation 1) it is reasonable to postulate as the rate-determining step for the isomerization of the alkylidenecycloalkanes, the abstraction of a proton from an allylic position.



Bromination of the cycloalkanones(II) was carried out as reported in the experimental section. The rates were first order in cycloalkanone. The results (at 0°) are shown in Table IV.

TABLE IV

RATE CONSTANTS AND RELATIVE RATES FOR CYCLOALKANONE BROMINATIONS

Ketone	Rate,[a] sec.$^{-1}$ × 10^4	Rel. rate (C_6 = 1)
C_4	45.3	15.5
C_5	29.6	9.9
C_6	3.0	1.0
C_7	5.0	1.7
C_8	10.0	3.4

[a] Pseudo-first-order rate constant in 0.0155 molar ketone and 0.100 molar base.

Enolization of the C_6-ketone is slow while the C_4-ketone enolization rate is faster than the C_5-ketone and both are faster than cyclohexanone. The C_7- and C_8-ketones also follow the same order as in the alkylidene-cycloalkane series. The C_8-ketone is brominated at a faster rate than the C_7-ketone and both are faster than cyclohexanone.

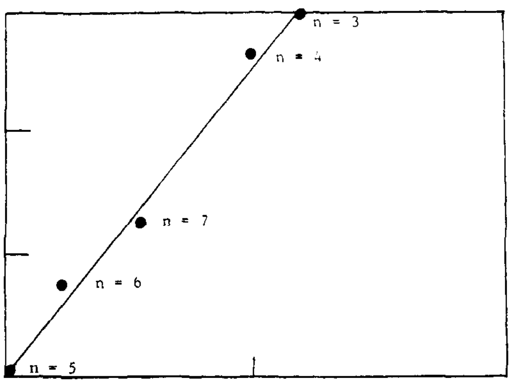


Fig. 2.—Log reaction rate for base-catalyzed isomerization of exocyclic olefins *vs.* log reaction rate for base-catalyzed ketone bromination.

The same minimum is again observed and, indeed, a plot of the log of the relative rate of double bond migration *vs.* the log of the relative rate of bromination is linear (Fig. 2). The average deviation of the points from the line is ±0.10 log unit on the abscissa and ±0.13 log unit on the ordinate. Since the range covered is almost four powers of 10 on the ordinate and over one power of 10 on the abscissa, a typical linear free-energy relationship seems to exist between the two reactions.

Discussion

The rate-determining step for base-catalyzed ketone bromination has been shown to be formation of the enolate ion.[15] Base-catalyzed olefin isomerization has been postulated to involve formation of a carbanion by proton abstraction as the rate-determining step (eq. 1).[13]

The linear free-energy relationship between the bromination and isomerization rates strongly suggests similar transition states and rate-determining steps for the two reactions. A reasonable conclusion is that the anionic isomerization of exocyclic olefins is controlled by the rate at which the α-hydrogen is removed by base, *i.e.*, by the acidity of the α-hydrogen. Acidity, in this phraseology, is a kinetic term and is related to the ease of proton abstraction by the base. Factors that stabilize the transition state relative to the ground state, or that destabilize the ground state relative to the transition state, will facilitate proton removal.

Corey[21] has noted that the energy of the transition state for enolization will be at a minimum when there is maximum opportunity for bond formation between the $sp^3 \rightarrow p$-orbital made available by the leaving hydrogen and the p-orbital of the carbonyl carbon. Because of the linear free-energy relationship with the cycloalkanones, an extension of this observation to the *exo-endo* double bond movement in the alkylidenecycloalkanes is evident. Furthermore, any factors that lead to ease of p-π-overlap in the transition state should increase reaction rate in both series. A profile of the path leading to the postulated transition state is depicted below. The p-orbitals may be considered to be either on the C=O or the C=C bonds.

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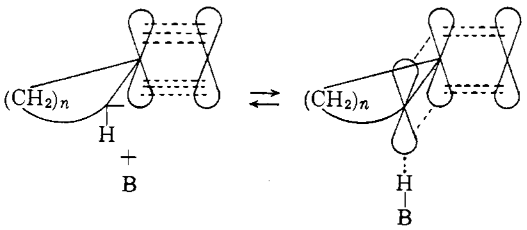
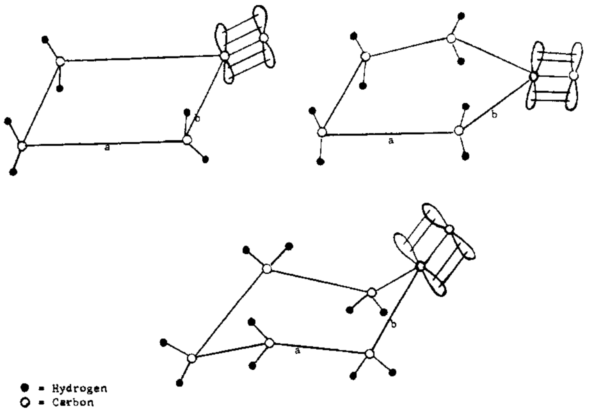
[21] E. J. Corey, *J. Am. Chem. Soc.*, **76**, 175 (1954).



Certainly the most striking phenomenon to be interpreted is the large *exo–endo* rate increase found in the four- and five-membered rings. The greater rate of methylenecyclopentane isomerization relative to that of methylenecyclohexane would seem to be in accordance with Brown's I-strain prediction.[4] It is difficult, however, to explain the rate of isomerization of methylenecyclobutane relative to that of methylenecyclopentane using internal strain concepts. I-strain would predict a slower rate for the four-membered ring isomerization due to an increase in "strain energy" brought about by formation of the carbanion whereas, in fact, the rate for methylenecyclobutane is faster.

A reasonable interpretation of the results for the entire series can be developed on the basis that rate is controlled by those situations that give rise to maximum p-π-overlap of the type previously discussed. In order to form an allylic anionic system, the rehybridizing p-bond in question has to be coplanar with the π-bond for maximum overlap. The developing p-orbital in the cyclohexane derivative is formed at an angle to the *exo* bond and, in order to rehybridize, a change has to occur in the geometry of the cyclohexane system since it is necessary for C–C bonds (a) and (b) in the figure below to be almost coplanar with the methylene or carbonyl group. Because this requires going from a more perfectly staggered conformation to a less perfectly staggered one, the change is resisted.

In the only slightly puckered C_5- and practically planar C_4-derivatives, however, less difficulty is encountered in bond rehybridization since C–C bonds (a) and (b) are already very nearly coplanar with the methylene or carbonyl group.[22,23]

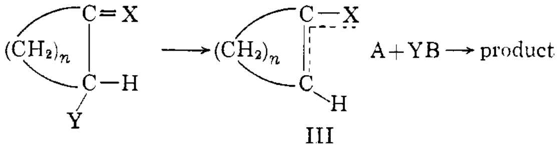


It is suggested that the main factor controlling the anionic reactions of the *exo-endo* double bond movement in the alylidenecycloalkanes and enolization in the cyclic ketones is the ease of rehybridization of the p-orbital on the α-carbon atom. The internal energy changes ($\Delta H^{\ddagger}$) for the C_4- and C_5-rings are markedly lower than those for the C_6-ring, indicating that a stabilization of the transition state such as that proposed is not unreasonable.

Models show that although the α-carbon atoms in the seven- and eight-membered rings are at relatively large angles to the allylic ring carbons, they are far less rigidly held than those of methylenecyclohexane and therefore in a better position to undergo the reorientation needed for p-π-bond formation. The large differences in $\Delta H^{\ddagger}$ between the 6- and the 7- and 8-rings bear this out. The high negative values of $\Delta S^{\ddagger}$ for the seven- and eight-membered rings relative to methylenecyclohexane support the observation of a less rigid ground state, more readily adaptable to the geometric requirements for p-π-rehybridization.

Inspection of Tables III and IV shows a striking difference in range of rates for olefin isomerization on one hand and ketone enolization on the other. The carbonyl oxygen in the cycloalkanones is a far stronger acceptor of electrons than the terminal allylic carbon in the alkylidenecycloalkanes. Because rehybridization is favored by resonance in the ketones, the activation energy for enolization will be lower than that for isomerization. It follows, therefore, that the range of rates for enolization should be smaller than that for isomerization.

Projection of Results to Similar Systems.—These results can be projected to other systems involving an allylic intermediate. For example, the same type of geometrical relationships should apply to the rehybridization that takes place during the formation of allylic cations and radicals. It is proposed, therefore, that anionic, cationic and radical reactions, involving α-substituents on compounds such as III, which proceed through an allylic transition state (as shown) will have comparable relative rates.



III

X = exocyclic substituent as C or O
Y = substituent on ring (Br, H, etc.)
A and B = positive-negative charge or radical

Acknowledgment.—The authors would like to acknowlege several original discussions with Professor H. C. Brown that led to portions of this research and many stimulating discussions with Professors W. von E. Doering, E. L. Eliel, and Dr. S. Bank, on the interpretation of the results. We would also like to thank Professor R. B. Turner of Rice University for supplying several olefins and Esso Research and Engineering Co. for permission to publish this research. We are grateful to Mr. Lars Naslund for working out the experimental details.

Experimental

Kinetic Procedure.—A dimethyl sulfoxide solution 0.744 molar in potassium *tert*-butoxide was prepared in a nitrogen-

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[22] A. I. Kitaygorodsky, *Tetrahedron*, **4**, 183 (1960).

[23] It is quite easy to see these relationships using Dreiding molecular models.

blanketed dry-box, equipped with a moisture conductivity cell. The solution was injected with a hypodermic syringe into a small vial, capped with a self-sealing neoprene stopper. The vial was preheated in a Fisher constant temperature bath (±0.5°) and prethermostated olefin (1.22 molar) was injected into the base–solvent mixture.

The vial was removed from the bath momentarily and shaken two or three times by hand to promote mixing. The homogeneous mixture was sampled periodically by withdrawing aliquots with a hypodermic syringe. To stop the reaction, the aliquot was injected into a bottle containing ice-water as well as a small amount of extraction agent (*n*-pentane for methylenecyclohexane, methylenecycloheptane and methylenecyclooötane isomerizations; *iso*-pentane for methylenecyclobutane and methylenecyclopentane isomerizations). The bottle was shaken and cooled to freeze the water–dimethyl sulfoxide mixture.

The supernatant pentane extract was analyzed on a Model 154 Perkin-Elmer gas chromatograph employing the following columns, temperatures and pressures. Methylenecyclobutane: DC-200, 59°, 15 p.s.i.; methylenecyclopentane: silver nitrate–diethylene glycol, 30°, 15 p.s.i.; methylenecyclohexane: 3% squalene on firebrick, 33°, 25 p.s.i.; methylenecycloheptane: silver nitrate–diethylene glycol, 30°, 15 p.s.i.; methylenecyclooötane: silver nitrate–diethylene glycol, 30°, 15 p.s.i. Two runs were made for each olefin. Kinetic data were reproducible to ±5%.

The experimental procedure outlined by Bartlett[16] was followed in the ketone brominations. One hundred cc. of a 0.1000 *N* standard sodium hydroxide solution, 100 cc. of distilled water, and 10 cc. of a 0.0155 *M* aqueous solution of the ketone were placed in a 250-cc. glass-stoppered flask and cooled to 0° (±0.5°). Ten cc. of separately cooled 0.0398 *M* bromine water was pipetted into the base-water-ketone solution to initiate the reaction. Aliquots of 25 cc. of the reacting solution were withdrawn periodically and added to 5 cc. of 0.3 *M* acetic acid solution containing an excess of solid sodium iodide, added just before the sample. The liberated iodine was titrated with thiosulphate. At least three runs were made for each ketone. Kinetic data were reproducible to ±2%.

Materials.—Potassium *tert*-butoxide was obtained from Mine Safety Appliance Co. This material was received as the sublimed, white powder. Analysis showed it to be above 98.5% pure, with K_2CO_3 as the major impurity. Dimethyl sulfoxide was dried and distilled over 13X molecular sieves (Linde). Infrared and mass spectrometric analysis showed it to be of high purity with little, if any, water. Gas chromatographic analysis indicated only one compound.

Methylenecyclobutane was obtained from Aldrich and purified by preparative gas chromatography. The resultant material was checked against a sample supplied by Professor R. B. Turner of Rice University. Methylenecyclopentane was obtained as an API standard. Methylenecyclohexane was obtained from Columbia Organic Chemicals Co. and checked against an API standard. Both methylenecycloheptane and methylenecyclooötane were prepared from their respective ketones by the Wittig reaction in rather low, *ca.* 5–10% overall yields. These materials were purified by preparative gas chromatography and characterized by infrared and n.m.r. techniques. In addition, the methylenecycloheptane was checked against an authentic sample supplied by Professor Turner. In all cases, the isomers showed only one peak on the gas chromatograph.

The *endo*-olefins 1-methylcyclobutene and 1-methylcycloheptene were supplied as reference samples by Professor Turner. The 1-methylcyclopentene and 1-methylcyclohexene were API reference samples. 1-Methylcyclooötene was identified by retention time on the gas chromatograph from the isomerization of methylenecyclooötane.

Cyclobutanone was obtained from Aldrich and was purified by preparative gas chromatography. An infrared spectrum of the resultant compound was checked against the reported spectrum. Cyclopentanone, cyclohexanone, cycloheptanone and cyclooötanone were purchased from Columbia Organic Chemicals Co. These were dried over 13X molecular sieves (Linde) and distilled to give a material that, in each instance, showed only one peak on the gas chromatograph.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

The Synthesis and Stability of Some Cyclopropenyl Cations with Alkyl Substituents[1]

BY RONALD BRESLOW, HERMANN HÖVER AND HAI WON CHANG

RECEIVED MARCH 7, 1962

The dipropylcyclopropenyl cation and the tripropylcyclopropenyl cation have been synthesized. Comparison of their *pK*'s shows that the alkyl groups have a considerable effect on the stability of the cyclopropenyl cation, and this is confirmed by a comparison of the *pK*'s of diphenylcyclopropenyl cation and propyldiphenylcyclopropenyl cation. The stabilization by propyl groups is even larger than that by phenyls, and this suggests that the alkyl effect is largely inductive. rather than hyperconjugative. N.m.r. studies reinforce this interpretation. By extrapolation the *pK* of unsubstituted cyclopropenyl cation can be estimated; the relationship between this estimate and the aromaticity of cyclopropenyl cation is discussed.

I. **Introduction.**—A number of aryl derivatives of the cyclopropenyl cation have recently been synthesized. The first such species, triphenylcyclopropenyl cation,[2,3] was found to be a stable carbonium ion, with pK_{R^+} 3.1, and subsequently salts of the diphenylcyclopropenyl cation[4] and of a series of *p*-methoxytriphenylcyclopropenyl cations[3] have been prepared.

The pK_{R^+}'s of these cations also have been determined, and the results can be correlated moderately well with the predictions of molecular orbital calculations.[3,4] Furthermore, both diphenylcyclopropenone[5] and dipropylcyclopropenone[6] have been synthesized. These ketones, and particularly their salts, may be considered to be derivatives of the cyclopropenyl cation as well.

The stability of these highly strained carbonium ions could at first sight be ascribed qualitatively to the substituents, since a large number of resonance forms can be written for the triphenylcyclopropenyl cation, for instance. However, it has already been shown that this effect alone cannot account for the observed stabilities, since the triphenylcyclopropenyl radical has considerably less

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(1) This work was supported by grants from the National Science Foundation, the Petroleum Research Fund and the Sloan Foundation. A preliminary report of some of this work was presented at the 17th National Organic Symposium, Bloomington, Ind., 1961, and by R. Breslow and H. Höver, *J. Am. Chem. Soc.*, **82**, 2644 (1960).

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