An Approach to a Benzocyclopropene[1]

BY EDWIN F. ULLMAN AND ERWIN BUNCEL

Attempts to generate the possibly aromatic dianions of Δ^3-carene-2,5-dione (VII) and 5,8-dimethoxy-2,3-methylene-1,2,3,4-tetrahydronaphthalene-1,4-dione (VIII) are described. Although neither the mono- nor dianions could be isolated, VIII was found to undergo facile deuterium exchange in CH_3ONa/CH_3OD or t-BuOK/t-BuOD, which is shown to occur exclusively via the monoanion. The data suggest that the carbanionic carbon atom of VIII$^-$ is non-planar. The strain energy of benzocyclopropene is estimated to be at least 45.5 kcal. greater than that of cyclopropane.

In light of the fact that the highly strained benzocyclobutene (I) is a stable isolable compound[2] and that benzyne (II), an even more highly strained species, has been shown to be present as a transient intermediate in numerous reactions,[3] it seemed probable that the missing middle member of this series, benzocyclopropene (III) should at least be capable of transient existence and quite probably could exist as a stable entity. Apart from the obvious desirability of exploring the chemistry of this missing member, the synthesis of this system would provide an opportunity to answer a number of intriguing questions. Thus it is possible that the methylene grouping in benzocyclopropene would lie out of the plane of the aromatic ring (cf. IV) as a consequence of the high ring strain of the planar configuration III would be largely localized at the bridge carbon atoms owing to distortion of the "normal" external bond angle of cyclopropene from $150°$[4] (cf. VI) to $120°$. If rehybridization of the bridge carbon atoms from sp^2 to sp^3 occurred, a complete relief of steric strain (excluding that of the three-membered ring itself) would be expected since the normal H–C–C cyclopropane bond angle[5] of $116°$ (cf. V) would then nearly coincide with the angle requirement in IV imposed by the six-membered ring ($120°$). Of course, complete rehybridization would have a strongly adverse
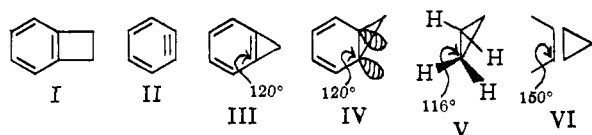
effect on the overlap and hence the energy of the aromatic π-electron system due to the divergence of the cyclopropene p-orbitals (cf. IV), but it might be expected that a partial, though probably small, rehybridization would minimize these two opposing forces, and hence would lead to a ground state geometry of the molecule in which the methylene group would lie slightly out of the plane of the aromatic ring in a configuration between the extremes represented by III and IV.

An additional feature of interest expected in benzocyclopropene is a partial fixation of the aromatic bonds due to the probable shortening of the bridge bond relative to the other aromatic C–C bonds, an effect which is expected by virtue of the observed shortening of the cyclopropene double bond (1.30 Å.)[4] compared to that of unstrained olefins (e.g., cis-2-butene, 1.38 Å.).[6]

This effect should lead to an alternation in bond lengths in the aromatic ring with decreased electron delocalization, and thus an increased tendency for the aromatic ring to react like a cyclohexatriene.[7]

The approach chosen for the synthesis of a benzocyclopropene was based on the hope that either the known carenedione (VII)[8] or the diketone VIII[9] could be converted to the corresponding dienolate and then alkylated. An examination of models revealed that
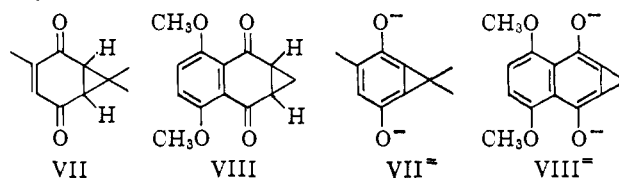
the initial step, formation of a monoenolate, might be expected to be very difficult since incorporation of a double bond at the bridgehead position would require exceptional distortion of bond angles.[10] Providing that enolization would occur at all, the resulting species might be of such high energy that it would undergo practically simultaneous loss of a second proton to the solvent affording both an increase in resonance stabilization due to aromatization and a decrease in strain energy.

Results

Because of the higher driving force for aromatization of a benzenoid system relative to aromatization of the second ring of a naphthalene,[11] 2-carene-1,4-dione (VII) was first chosen for study. However, perhaps not surprisingly, the compound proved to be very labile in alkaline media with the formation of highly colored decomposition products. Treatment of VII with 0.35 N sodium ethoxide in ethanol under the most strenuous conditions which permitted its recovery (3 minutes at $-10°$) did not lead to measurable enolization toward the cyclopropane. Thus quenching of the reaction

(7) A similar prediction of bond alternation has been made for benzyne: C. A. Coulson, "Chemical Society Symposia, Spec. Publ. No. 12," The Chemical Society, London, 1958, p. 85.

(8) E. J. Corey and H. J. Burke, J. Am. Chem. Soc., **78**, 174 (1956).

(9) J. F. Garden and R. H. Thomson, J. Chem. Soc., 2851 (1957).

(10) Although deuterium exchange at cyclopropyl bridgehead positions has previously been observed in carones i and ii, the saturated six-membered rings in these compounds confer considerably greater flexibility than is present in VII or VIII, and the increase in strain on introduction of a double bond at a bridgehead position may not be prohibitively large: G. Büchi, M. S. v. Wittenau and D. W. White, J. Am. Chem. Soc., **81**, 1968 (1959).

(1) Unsaturated Cyclopropanes, IV; for paper III see E. F. Ullman and W. J. Fanshawe, J. Am. Chem. Soc., **83**, 2379 (1961).

(2) M. P. Cava and D. R. Napier, ibid., **78**, 500 (1956); **80**, 2255 (1958).

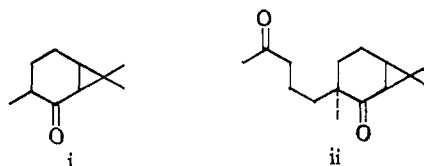(3) See R. Huisgen and J. Sauer, Angew. Chem., **72**, 91 (1960), for leading references.

(4) P. H. Kasai, R. J. Myers, D. F. Eggers, Jr., and K. B. Wiberg, J. Chem. Phys., **30**, 512 (1959).

(5) O. Bastiansen and O. Hassel, Tidsskr. Kjemi, Bergvesen Met., **6**, 71 (1946); Chem. Abstr., **40**, 6059 (1946).

(6) L. O. Brockway and P. C. Cross, J. Am. Chem. Soc., **58**, 2407 (1936).

(11) Compare the resonance energy of benzene, 36 kcal., to the additional naphthalene resonance energy over that of benzene of only 25 kcal.: G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 98.

mixture with acidic D_2O led to only 1.5% incorporation of deuterium which was shown by mass spectrometric analysis to have entered in the 2-methyl group.
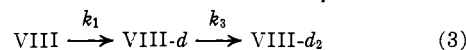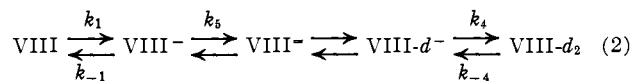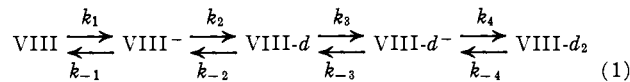
In contrast, it had been reported that the diketone VIII can be recovered unchanged from hot aqueous alkali,[9] thus making it a more likely candidate for our investigation. Initially an attempt was made to observe the dianion VIII= directly by n.m.r. A solution of VIII in CD_3OD showed the expected peaks at 2.58 τ (singlet, aromatic), 6.19 τ (singlet, OCH_3), 7.37 τ (multiplet, tertiary cyclopropyl) and 8.43 τ (multiplet, cyclopropyl methylene) which, however, were unchanged upon dissolution of a piece of sodium in the solution. Although increasing the temperature of the solution to 100° still failed to show any change, when the solution was maintained at this temperature for one hour all the peaks in the spectrum except the cyclopropylmethylene peak were observed to diminish in intensity with the tertiary cyclopropyl hydrogens disappearing fastest followed by the O–methyl peak and, more slowly, the aromatic proton peak. Simultaneously, increased absorption appeared due to CD_3OH and a new sharp peak developed on top of the solvent CHD_2OD multiplet that was shown to be due to CH_3OD. In confirmation of these results a mass spectrum of the recovered VIII showed that up to ten deuteriums had been incorporated. Thus not only had the cyclopropyl hydrogens exchanged but there was also both an unexpectedly facile nucleophilic aromatic displacement of methoxide by CD_3O^- and exchange on the aromatic ring.[12] Longer treatment of VIII with 3.8 M sodium methoxide in methanol led to its eventual reduction to give the ketol IX, which could be prepared alternatively by treatment of VIII with one equivalent of sodium borohydride.

Trapping experiments were next conducted to establish whether any conditions might be found in which a significant concentration of the dianion VIII= was present. Thus VIII was treated with increasingly stronger bases, sodium methoxide in methanol, potassium t-butoxide in t-butyl alcohol, potassium t-butoxide in dimethyl sulfoxide, sodamide in liquid ammonia and lithium diethylamide in anisole, under the most vigorous conditions which would permit recovery of VIII from each medium, and the resulting mixtures were quenched with excess dilute D_2SO_4 in D_2O. However, even after treating VIII for eight hours with sodamide in liquid ammonia at −33° or 45 minutes with lithium diethylamide in anisole at 50°, the mass spectra of recovered purified samples showed neither monodeuterated (≤0.7%) nor dideuterated (≤0.6%) VIII, indicating the absence of appreciable concentrations of either the mono- or dianion even under these highly alkaline conditions.

The possibility remained, however, that the dianion of VIII was in fact formed under some or all of these conditions, but that it decomposed as rapidly as formed so that a significant concentration could not accumulate. To test this possibility, exchange experiments were carried out with sodium methoxide in deuteriomethanol and potassium t-butoxide in deuterio-t-butyl alcohol, and the purified recovered diketone analyzed by mass spectrometry for the ratios of non-, mono- and dideuterated components. Providing the dianion was

formed and survived at least long enough to be reprotonated, it would then be expected that dideuterated diketone VIII-d_2 would be recovered in excess of that predicted by the stepwise exchange process 1 because of competition from process 2 involving the dianion VIII=. Thus if dilute solutions and highly deuterated solvents are used so that k_{-1} and k_{-3} are small, exclusive operation of process 1 would lead to a rapid increase in the percentage of monodeuterated diketone VIII-d followed by a slower build-up of the dideuterated compound VIII-d_2, while process 2 would lead to the exclusive formation of VIII-d_2.

$$\text{VIII} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{VIII}^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{VIII-}d \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{VIII-}d^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \text{VIII-}d_2 \quad (1)$$

$$\text{VIII} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{VIII}^- \overset{k_5}{\rightleftharpoons} \text{VIII}^= \rightleftharpoons \text{VIII-}d^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \text{VIII-}d_2 \quad (2)$$

$$\text{VIII} \overset{k_1}{\longrightarrow} \text{VIII-}d \overset{k_3}{\longrightarrow} \text{VIII-}d_2 \quad (3)$$

The kinetic expression for the exchange process 1 is derived from the assumptions: (a) The pseudo-first-order rate constants for the proton (or deuteron) abstraction steps k_1, k_{-2}, k_3 and k_{-4}, are slow relative to the protonation rates k_{-1}, k_2, k_{-3} and k_4 and hence are rate determining. (b) The rates of protonation and deuteration of VIII$^-$ and VIII-d^- are solely a function of the isotopic content of the solvent, which is effectively constant at the concentrations used, and thus $k_{-1} = k_{-3}$ and $k_2 = k_4$. (c) Secondary isotope effects on rates k_3 and k_{-4} would be small[13] and are ignored. Any error resulting from their omission would tend to increase the expected percentage of VIII-d_2 from sequence 1 and hence would not lead to a false assumption of the intermediacy of the dianion VIII=. (d) Statistically it is required that $k_1/k_3 = k_{-4}/k_{-2} = 2$.

Since the sodium methoxide exchange experiments were conducted with deuteriomethanol of <1% protium content, we may neglect the protonation steps k_{-1} and k_{-3} and, with the above assumptions, the reaction becomes kinetically equivalent to 3 for which eq. 4 may be used,[14a] where α, β and γ represent the fractions of VIII, VIII-d and VIII-d_2, respectively, in the product and $\tau = k_1 t$.

$$\alpha = e^{-\tau}, \ \beta = 2(e^{-\tau/2} - e^{-\tau}), \ \gamma = 1 - (\alpha + \beta) \quad (4)$$

Table I gives the results of two runs in which VIII was heated for about 23 and 42 minutes, respectively, with a 3.5 M sodium methoxide solution in deuterio-

TABLE I

METHOXIDE-CATALYZED EXCHANGE OF VIII[a]

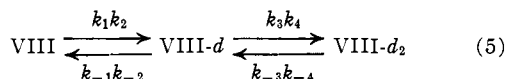| Isotopic component	Run 1[b]		Run 2[c]	
	Found[d]	Calcd.	Found[d]	Calcd.
α (VIII)	0.356	...	0.172	...
β (VIII-d)	.481	0.480	.486	0.488
γ (VIII-d_2)	.162	0.163	.342	0.340

[a] 3.5 M CH_3ONa in refluxing CH_3OD. [b] 23 minutes. [c] 42 minutes. [d] Adjusted for aromatic hydrogen exchange as measured by 1.1 and 4.1% trideuteration in runs 1 and 2, respectively.

methanol. Since the method used did not permit direct comparison of the reaction times, the two runs were calculated independently, the value found for α in each case being used to determine τ (eq. 4). Although the very close fit of the data is perhaps fortuitous since secondary isotope effects have been ignored, there is clearly no excess of VIII-d_2 (γ) over the predicted percentages.

(12) The smooth exchange of aromatic methoxyl groups in VIII (40–84% exchange had occurred under these conditions) is not expected for simple alkoxy phenyl ketones as is seen by the fact that bis-p-methoxybenzophenone undergoes only about 4% exchange of methoxyl and <0.2% exchange of aromatic hydrogen after 2.5 hours under comparable conditions; unpublished observation. The marked reactivity of VIII probably is due to the combination of several factors, the most important possibly being the additive effect of two carbonyl substituents on charge stabilization, even though one of these cannot directly accommodate a charge because of its orientation *meta* to the displaced group.

(13) A k_H/k_D ratio of no more than about 1.04 is expected for the secondary β-deuterium isotope effect: A. Streitwieser, Jr., and D. E. Van Sickle, *J. Am. Chem. Soc.*, **84**, 254 (1962).

(14) (a) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 154; (b) p. 163.

A similar exchange study using potassium t-butoxide in deuterio-t-butyl alcohol was complicated by the use of incompletely deuterated solvent (7.5% protium by n.m.r. analysis) which allowed the reverse reactions to become kinetically significant. Accordingly, the equilibrium constant K_2 = VIII-d_2/VIII-d = 4.20 was first determined from the mass spectrometrically estimated ratios of deuterated VIII (Table II, runs 1 and 2) recovered after complete equilibration with 0.2 M potassium t-butoxide in deuterated t-butyl alcohol. With K_2 known, process 1 can then be treated as the simple

$$\text{VIII} \underset{k_{-1}k_{-2}}{\overset{k_1k_2}{\rightleftharpoons}} \text{VIII-}d \underset{k_{-3}k_{-4}}{\overset{k_3k_4}{\rightleftharpoons}} \text{VIII-}d_2 \qquad (5)$$

equilibrium 5 where $K_2 = k_3 k_4/k_{-3} k_{-4}$ and from b and d above, $K_1 = k_1k_2/k_{-1}k_{-2} = 4K_2{}^{15}$ and $k_1k_2 = 2k_3k_4$. The kinetic treatment for this type of equilibrium has been described previously[14b]; substitution into the equations gives 6 in which $\tau = k_{-1}k_{-2}(2K_2 + 1)t$.

$$\alpha = \left(\frac{2K_2e^{-\tau} + 1}{2K_2 + 1}\right)^2, \quad \beta = \frac{4K_2\alpha(1 - e^{-\tau})}{2K_2e^{-\tau} + 1},$$
$$\gamma = 1 - (\alpha + \beta) \quad (6)$$

Runs 3 and 4 in Table II give the ratios of non-, mono- and dideuterated VIII of samples recovered after partial equilibration of VIII. As before, the ex-

TABLE II
t-BUTOXIDE-CATALYZED EXCHANGE OF VIII[a]

Isotopic component	Run 1[b] Found[f]	Run 2[c] Found[f]	Run 3[d] Found	Run 3[d] Calcd.	Run 4[e] Found	Run 4[e] Calcd.
α (VIII)	0.015	0.011	0.200	...	0.942	...
β (VIII-d)	.191	.189	.507	0.495	.057	0.058
γ (VIII-d_2)	.794	.800	.293	0.305	.001	0.000

[a] 0.2 M t-BuOK in t-BuOD at 50°. [b] 20 hours. [c] 4.75 hours [d] 1 hour. [e] 75 seconds. [f] Adjusted for aromatic hydrogen exchange as measured by 10.7 and 2.2% trideuteration in runs 1 and 2, respectively.

perimental value for α was used in each case to determine τ, from which β and γ could be calculated. A close fit of the experimental ratios with the ratios expected for exclusive sequential exchange of hydrogen is again found. Thus, at least with methoxide and t-butoxide, either the rate of removal of a second proton from VIII$^-$, k_5 (eq. 2), is much slower than the rate of reprotonation, $k_{-1} + k_2$, or the dianion VIII$^=$ is so exceedingly unstable that it decomposes even faster than it can abstract a proton from the solvent. The latter possibility, however, is very unlikely considering the high stability of VIII toward much stronger bases (vide supra).

Although all attempts to trap or detect the dianion VIII$^=$ by deuterium exchange were unsuccessful, the fact that exchange of the cyclopropyl hydrogens did occur suggested the possibility of trapping the anion by

IX   X   XI   XII
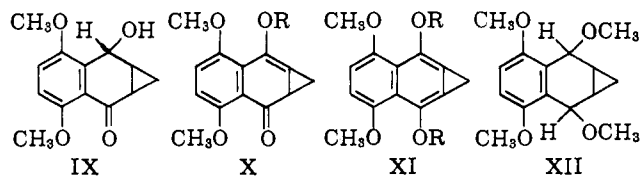
O-alkylation. The resulting highly strained enol ether X might then undergo loss of a second proton followed by alkylation to give the desired tetraalkoxynaphthalene (XI). Since this scheme requires the simultaneous presence of both base and alkylating agent, a solution of VIII in dimethoxyethane containing excess methyl iodide was refluxed over sodium hydride. Although reac-

tion occurred, the resulting product proved to be the reduced tetraether XII as shown by the absence of either hydroxyl or carbonyl absorption in the infrared and the appearance in the n.m.r. of a new methoxyl peak at 6.58 τ and a multiplet (quartet?) centered at 4.96 τ corresponding to the benzyl hydrogens. The sharpness of the new methoxyl peak suggests that the two aliphatic methoxyls are identical and thus are cis-oriented, the benzyl multiplet possibly being the A part of an A_2X_2 pattern in which the cyclopropyl X protons are further coupled with the methylene protons and are unresolved (8.3–9.3 τ).

On the basis of the earlier observation that long treatment of VIII with sodium methoxide leads to reduction of a carbonyl group, we postulate that VIII is reduced by methoxide generated by the action of sodium hydride on the solvent.[16] The resulting diol might then undergo alkylation to give the observed product. An attempt to circumvent this difficulty by using methyl iodide itself as the solvent was unsuccessful; only a small amount of gas was evolved and the starting material was recovered unchanged.

Discussion

If it is assumed that the isotopic composition of the diketone VIII recovered from the quenching experiments reflects the true equilibrium position between VIII and its mono- and dianions, it is possible to make a crude estimate of the minimum excess strain energy of VIII$^=$ over that of VIII itself. This may be done by comparing the equilibrium constant for the model ketone–diphenolate equilibrium

$$\qquad (7)$$

XIII   XIII$^=$
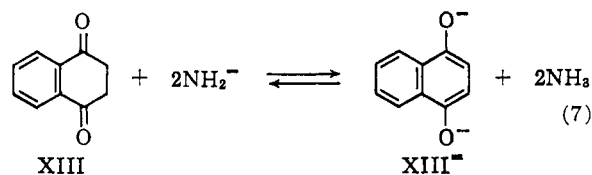
with the maximum constant for the equilibrium between VIII and VIII$^=$ consistent with the present data. Since a fair estimate of the base strength of amide ion in liquid ammonia is available (pK_a = 39 at −33°),[17] data from the runs using sodamide as the base are employed.

The pK_a of XIII may be calculated from the acidity constants of the tautomeric naphthalene-1,4-diol (K_1 = 3 × 10^{-11}, K_2 = 1.6 × 10^{-12})[18] and the equilibrium constant between XIII and the diol. A minimum value for the latter (K = 10) is derived from the observation[19] that the diol is in equilibrium with about 10% of the diketone XIII at 210°, although the constant is probably considerably greater at lower temperatures. We thus obtain a minimum acidity constant product of 5 × 10^{-22} for the removal of both protons from XIII or an equilibrium constant $K_{XIII} \geq 5 \times 10^{56}$ for reaction 7 in liquid ammonia at −33°.

Based on the maximum percentage (0.6%) of dideuterated VIII obtained on quenching sodamide-equilibrated solutions with D$_2$SO$_4$, the equilibrium constant[19a] K_{VIII} for 8 can be no greater than 2 × 10^4.

(16) Treatment of methyl iodide alone with sodium methoxide in dimethoxyethane led to a slow evolution of hydrogen, suggesting attack of hydride on the solvent. In addition, a considerable amount of methane from reduction of the halide was evolved.

(17) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p. 88.

(18) Estimated by extrapolation to −33° of the acidity data of J. H. Baxendale and H. R. Hardy, Trans. Faraday Soc., 49, 1140 (1953).

(19) R. H. Thomson, J. Chem. Soc., 1737 (1950).

(19a) Calculated on the basis of [NH₃] = 46.5, [NH₂⁻] = 0.025 and [VIII⁻]/[VIII] ≤ 0.006 (see Table III). Thus, K_{VIII} = [VIII⁻][NH₃]²/[VIII][NH₂⁻]² ≤ 2 × 10⁴.

(15) Although K_1 may be obtained directly (Table II, runs 1 and 2, K_1 = β/α), the uncertainty in the small experimental value of α made it preferable to calculate K_1 from K_2.

$$VIII + 2NH_2^- \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{1cm}{0pt}}} VIII^= + 2NH_3 \qquad (8)$$

Since the entropy changes for the two closely related processes 7 and 8 should be roughly equivalent, the difference between the free energy changes, as derived from the equilibrium constants, can be taken as a rough estimate of the excess strain energy of $VIII^=$ over that of VIII. Thus we obtain the surprisingly high value of at least 57.6 kcal. for the strain energy of a benzocyclopropene in excess of the strain in a saturated cyclopropane.

For comparison, the expected strain energy of benzocyclopropene can be estimated from available thermal data. We may obtain first the excess strain introduced on converting a cyclopropane into a cyclopropene, and then add to this the estimated additional energy per mole needed to distort two external (C=C—C) cyclopropene bond angles from their normal 150° angles (cf. VI) to 120° required by benzocyclopropene (cf. III). Since the over-all transformation requires practically no net change in the external angles to the three-membered ring (cf. V and III), we may ignore to a first approximation the mutual repulsion of the carbonyl groups attached to the ring and use as a model cyclopropene itself which has been estimated to have an excess strain energy of 27 kcal. over that of cyclopropane.[20]

The energy needed to distort from 150° to 120° the two C=C—C bond angles formed by the cyclopropene double bond and each substituent (e.g., VI → III) cannot of course be found directly. It is, however, possible to estimate the strain energy needed to cause a distortion of similar magnitude (30°) of a cis-olefin from its normal C=C—C bond angles of 120° to 90° while ignoring the non-bonded repulsions of the olefinic substituents for the already-described reason. Thus the strain energy for such a distortion can be roughly estimated from the sum of the strain energy associated with two of the methylene groups of cyclobutane (13 kcal.) and that associated with the introduction of a double bond into a four-membered ring (5.5 kcal.). The former is half the strain energy of cyclobutane (26 kcal.)[21] and the latter is estimated from the difference in the known heats of hydrogenation of 1-methylcyclobutene (28.5 kcal.)[22] and 1-methylcyclopentene (23.0 kcal.).[23] The resulting strain energy of 18.5 kcal. is for an approximate 30° distortion of two *normal* cis-olefin C=C—C bond angles where the remaining two olefinic substituents are allowed to move to their most stable configurations in which they form an angle of about 141° with the double bond, the approximate cyclobutene H—C=C bond angles.[24] In contrast, the strain for a similar 30° distortion of the external C=C—C bond angles of a cyclopropene cannot be compensated by a reorientation of the remaining olefinic substituents which are now part of the ring, and thus 18.5 kcal. probably represents the minimum strain energy required for this process.

Thus, from thermal data we obtain a strain energy for benzocyclopropene of 27 kcal. for introduction of a double bond into a three-membered ring plus at least 18.5 kcal. for a 30° distortion of the two external cyclopropene C=C—C bond angles, or a total estimated strain energy of no less than 45.5 kcal. In contrast, we have estimated from the experimental data a minimum of 57.6 kcal. excess strain energy of $VIII^=$ over that of VIII.

(20) K. B. Wiberg, W. J. Bartley and F. P. Lossing, *J. Am. Chem. Soc.*, **84**, 3980 (1962).

(21) Sj. Kaarsemaker and J. Coops, *Rec. trav. chim.*, **71**, 261 (1952).

(22) R. B. Turner, "Theoretical Organic Chemistry," Kekulé Symposium, Butterworth, London, 1959, p. 67.

(23) R. B. Turner and R. H. Garner, *J. Am. Chem. Soc.*, **80**, 1424 (1958).

(24) E. Goldish, K. Hedberg and V. Schomaker, *ibid.*, **78**, 2714 (1956).

Two possibilities may be considered to explain this difference. First it is conceivable that our estimate of the effect of distorting the external C=C—C bond angles of cyclopropene is sufficiently low to account for 12 kcal. error. Although we are unable to exclude this possibility, the error may be compensated to some extent by the possible relief of strain that may be available to VIII by some distortion of the methylene out of the plane of the aromatic nucleus (vide supra). Second, it is possible that our experimental minimum strain energy is misleading and that the dianion $VIII^=$ is actually favored thermodynamically over VIII in sodamide–liquid ammonia solution, but that the rate of removal of a proton from $VIII^-$ (k_5 in sequence 2) is so much slower than the rate of reprotonation of this species (k_{-1}) that an undetectable amount of dianion is formed during the course of the reaction. Unfortunately, direct evidence on this point was not obtainable as it was not possible to increase the time of the sodamide reactions above about 8 hours due to slow decomposition of the diketone and use of lithium diethylamide required even shorter reaction times. However this explanation is plausible in that reprotonation of the highly basic monoanion $VIII^-$ (k_{-1}) would be expected to be very fast while proton abstraction (k_5) would be fast only if further ionization of $VIII^-$ were strongly favored as would be the case if most of the strain had already been introduced upon abstraction of the first proton. The behavior of VIII would then be comparable to that of the diketone XIII in which the first acidity constant is probably similar to that of propiophenone ($pK_a \sim 21$)[25] while the monoanion is then calculated to be a very strong acid ($pK_a \sim 0.3$) and presumably is formed and ionizes practically simultaneously.

In order to compare the strain energies of VIII and of the monoanion $VIII^-$ we first calculate from the maximum percentage (0.7%) of VIII-d, obtained on quenching sodamide-equilibrated solutions with D_2SO_4, a maximum equilibrium constant of 13 for reaction 9.

$$VIII + NH_2^- \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{1cm}{0pt}}} VIII^- + NH_3 \qquad (9)$$

Comparison then with the estimated equilibrium constant of about 10^{16} for the ionization of isobutyrophenone[25] in the same medium leads to a calculated energy difference of about 16.4 kcal. between the two processes. As before, we assume that the entropies of ionization of VIII and the model will be very similar, so that we obtain a minimum value of only 16.4 kcal. for the strain energy of the monoanion $VIII^-$ in excess of the strain of VIII itself. Thus the experimental evidence permits no conclusion to be drawn on whether $VIII^-$ might have similar or greater strain energy than $VIII^=$, and hence no deduction regarding the relative values of k_{-1} and k_5 may be made in this way.[26] On the other hand, the rapid rate of deuterium exchange of VIII with even a relatively weak base such as methoxide perhaps suggests that the monoanion $VIII^-$ does indeed have substantially less strain energy than the enormous 45.5 kcal. estimated for $VIII^=$, and thus it seems probable that equilibrium conditions were not achieved in our quenching experiments

(25) Although the acidities of propiophenone and isobutyrophenone have not been measured, approximate values may be obtained from the known pK_a of 19 for acetophenone (W. K. McEwen, *ibid.*, **58**, 1124 (1936)) and the pK_a difference of 2 between butyrophenone and α-ethylbutyrophenone (W. L. Rellahan, W. L. Gumby and H. D. Zook, *J. Org. Chem.*, **24**, 709 (1959)). Assuming a similar pK_a difference for propiophenone and isobutyrophenone and between acetophenone and propiophenone, we obtain a pK_a of 21 for propiophenone and 23 for isobutyrophenone.

(26) The strain in $VIII^-$ is, however, substantially in excess of that arising by ionization of a normal cyclopropylketone since, in contrast to VIII, benzoylcyclopropane may be readily converted to its enolate with sodamide; F. J. Piehl and W. G. Brown, *J. Am. Chem. Soc.*, **75**, 5023 (1953).

and that the experimental strain energy estimate of 57.6 kcal. is in error.

Despite the rapid rate of exchange of VIII, models of VIII⁻ suggest that it is much more strained than the dianion VIII⁼ because of strong torsional restrictions against planarity of the enolate. Examination of models of VIII, however, shows that only a modest distortion of the carbonyl oxygens out of the plane of the aromatic ring (cf. XIV) can place the tertiary C–H bonds coplanar, although not parallel, with the p-orbitals of the adjacent carbonyl carbon atoms. If
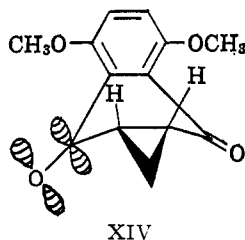
XIV

then, upon abstraction of a proton, the original tetrahedral configuration of the tertiary cyclopropyl carbon is unchanged, partial overlap of the resulting sp³-hybridized carbanionic orbital and the carbonyl π-orbital might provide sufficient stabilization to account for the rapid deuterium exchange without formation of the exceptionally strained planar enolate.

It is noteworthy that a recent study of the relative rates of exchange and racemization of 2,2-diphenyl-cyclopropylnitrile has lead to the suggestion that this compound may also form a non-planar carbanion.[27]

Experimental

Materials.—Δ³-Carene-2,5-dione[8] (VII) and 5,8-dimethoxy-2,3-methylene-1,2,3,4-tetrahydronaphthalene-1,4-dione[9] (VIII) were prepared according to literature procedures and recrystallized to constant melting point; VII, m.p. 93–94°; VIII, m.p. 168–169°. The ultraviolet, infrared and n.m.r. spectra were in complete accord with the assigned structures. Methanol-d_4 was used without purification[28] and may not have been dry. The methanol-d was dried by distillation from magnesium methoxide to give a product containing >99% CH₃OD by n.m.r. analysis. The deuterio-t-butyl alcohol was prepared by the addition of D₂O to freshly prepared dry potassium t-butoxide. After drying the distilled solvent over calcium hydride and redistilling, the product so obtained was 92.5% deuterated by n.m.r. analysis. Non-deuterated solvents were purified and dried by conventional methods.

Effect of D₂SO₄ Quenching of Alkaline Solutions of Δ³-Carene-2,5-dione (VII).—The diketone VII proved to be very sensitive to bases and produced deep red solutions with aqueous sodium hydroxide or sodium methoxide in ethanol under nitrogen. By working at −10° it was found possible to reisolate some of the diketone from 3.5 M sodium ethoxide in ethanol by pouring the solution into dilute D₂SO₄ after 3 minutes reaction time. The mass spectrum of the recrystallized product indicated a maximum of 1.5% monodeuteration had occurred which appeared to have been on a methyl group by the absence of a peak corresponding to VII-d less a methyl group ($m/e = 150$).

Treatment of 5,8-Dimethoxy-2,3-methylene-1,2,3,4-tetrahydronaphthalene-1,4-dione (VIII) with Bases. A. Sodium Methoxide in Tetradeuteriomethanol.—No change in the n.m.r. spectrum of a solution of 15 mg. of VIII in 0.4 ml. of CD₃OD was observed on dissolving about 20 mg. of sodium in the solution. The resulting solution on slowly warming to 60° over 1 hour still showed no change, but on heating at 100° for another hour the t-cyclopropyl peaks completely disappeared along with a decrease in intensity and resolution of the aromatic hydrogen absorption. Simultaneously a new sharp peak appeared which increased in intensity on addition of methanol.

Addition of dilute acid to the resulting solution and extraction with ether gave, after evaporation of the extracts, a residue of the starting diketone which on recrystallization from methanol melted at 167°. Mass spectrometry showed the parent mass peaks (percentages in brackets) at: 234 (0.3), 235 (0.4), 236 (1.2), 237 (4.6), 238 (4.3), 239 (12.5), 240 (41.5), 241 (27.8),

242 (6.7) plus 0.7% at 243 possibly due to a trace of deuterated IX not removed on recrystallization.

B. Sodium Methoxide in Methanol.—A solution of 100 mg. of VIII in 4 ml. of 3.0 M sodium methoxide in methanol was refluxed under nitrogen for 5 hours and a 1-ml. aliquot added to 5 ml. of 1 M D₂SO₄ at 0°. The crude product isolated by chloroform extraction was twice recrystallized from methanol to give 10 mg. (40%) of IX, m.p. 207–209°, which showed new hydroxyl absorption in the infrared (CHCl₃) at 2.90 μ. The n.m.r. spectrum displayed singlets at 6.14 and 6.18 τ (OCH₃), a doublet centered at 7.43 τ (OH) and multiplets at 4.39 τ (ArCH), 7.76 τ (t-cyclopropyl) and 8.99 τ (sec-cyclopropyl).

Anal. Calcd. for C₁₃H₁₄O₄: C, 66.65; H, 6.02; mol. wt., 234. Found: C, 67.24; H, 5.78; mol. wt. (mass spec.), 234.

The same compound was also formed by heating 0.23 g. of VIII in 15 ml. of anhydrous isopropyl alcohol containing 0.25 equiv. of sodium borohydride at 55° for 1.5 hours. The cooled solution was treated with dilute acid and then extracted with chloroform. The residue obtained on evaporation of the extracts yielded, after several recrystallizations from methanol, 0.03 g. of IX, identical in all respects with the previously obtained sample.

C. Quenching Experiments.—The diketone VIII was treated under nitrogen with the various bases summarized in Table III. The solutions were quenched by pouring into excess dilute D₂SO₄ in D₂O, and the recovered diketone was purified by recrystallization from methanol. The small parent mass peaks at $m/e = 233$ and 234 in the mass spectra of the recovered samples represent the *maximum* percentages of VIII-d and VIII-d_2 present in the samples, and probably may arise in part from trace impurities since the mass spectra of the mother liquors of the recrystallized samples generally showed increased percentages of these masses.

TABLE III

PERCENTAGE DEUTERATION OF VIII BY D₂SO₄ QUENCHING OF ALKALINE SOLUTIONS

				Isotopic component		
Base	[VIII], m./l.	Time, min.	T, °C.	232	233	234
3 M CH₃ONa/CH₃OH	0.107	30	65	100.0	...	...
1 M t-BuOK/t-BuOH	.057	330	50	99.2	...	0.8
1 M t-BuOK/t-BuOH	.057	1680	50	97.6	0.7	1.6ᵃ
0.5 M t-BuOK/DMSO	.107	0.75	15	ᵇ		
.25 M Et₂NLi/(CH₃OCH₂–)₂	.027	210	80	99.4	0.4	0.2
.5 M Et₂NLi/PhOCH₃ᶜ	.071	45	50	98.9	0.5	0.5
.025 M NaNH₂/liq.NH₃ᵈ	.010	480	−33	98.7	0.7	0.6

ᵃ Impure sample, m.p. 150–160°. ᵇ Rapid decomposition prevented recovery of crystalline material. ᶜ Et₂NLi only partially dissolved. ᵈ Reaction quenched by evaporation of the solvent and addition of dilute D₂SO₄ to the residue.

D. Equilibration with Deuterated Solvents.—Solutions of VIII were equilibrated under nitrogen by immersion of the flasks, equipped with reflux condensers, in oil-baths maintained at 80° and 50° for the CH₃OD and t-BuOD runs, respectively. Aliquots of the resulting solutions were removed at intervals, and the diketone recovered by dilution with aqueous acid followed by extraction with chloroform. The residues obtained on evaporation of the extracts were recrystallized to constant melting point.

Tables I and II give the exact experimental conditions for each run and the ratios of non-, mono- and dideuterated VIII in the products determined by mass spectrometry. As a cross check against the mass spectral results, the total percentages of deuteration at the t-cyclopropyl carbon in the products of the two methoxide runs (Table I) were also obtained by integration of the n.m.r. curves. The percentages as determined by mass spectrometry were 40.2% and 58.5% for runs 1 and 2, respectively, which were in good accord with the somewhat less accurate percentages of 39% and 62%, respectively, determined by n.m.r.

Since a carefully regulated constant temperature bath was not used in this work and no special care was taken to prevent loss of solvent during the course of a run, the reaction times given in the tables were not used in the calculations. Rather, the fraction of each product represented by undeuterated VIII was used to calculate the expected ratios of the other two components, VIII-d and VIII-d_2.

Attempted Alkylation of 5,8-Dimethoxy-2,3-methylene-1,2,3,4-tetrahydronaphthalene-1,4-dione (VIII).—To 0.48 g. of sodium hydride was added a solution of 1.24 ml. of methyl iodide and 0.180 g. of the diketone VIII in 7.5 ml. of dimethoxyethane. After stirring for 19 hours at room temperature, the mixture was filtered and the filtrate evaporated *in vacuo*. The residue was taken up in water and extracted with ether. Evaporation of the extracts gave, after crystallization from methanol–carbon tetrachloride, 0.040 g. of XI, m.p. 124.5–125.5°.

Anal. Calcd. for C₁₅H₂₀O₄: C, 68.16; H, 7.63; mol. wt., 264. Found: C, 68.06; H, 7.15; mol. wt. (mass spec.), 264.

(27) H. M. Walborsky, A. A. Youssef and J. M. Motes, *J. Am. Chem. Soc.*, **84**, 2465 (1962).

(28) Supplied by Merck and Co., Ltd., Montreal, Can.

Anionic Activation of C–H Bonds in Olefins. V. Influence of Structure on Reaction Rate

BY A. SCHRIESHEIM, C. A. ROWE, JR., AND L. NASLUND

The base-catalyzed proton migration rates of a series of terminal olefins of varying structure were studied in a homogeneous system using potassium *tert*-butoxide–dimethyl sulfoxide between 35 and 55°. The steric and electronic effects of substituents on four classes of olefinic structures were studied. It was found that the effect of substitution of the various alkyl groups for hydrogen gave rise to the same change in rate in each series. Correlations employing a Taft–Hammett type treatment show that both the inductive and steric effects of the alkyl groups are important. It has also been shown that the ease of reaching a coplanar transition state plays a large role in determining the C–H bond activity of acyclic olefins. In addition, electron delocalization effects are quite important in these prototropic shifts and a comparison of steric, inductive and electron delocalization effects is made.

Several recent papers have discussed the anionic activation of allylic C–H bonds[1a–d] for prototropic migrations in olefinic hydrocarbons in potassium *tert*-butoxide–dimethyl sulfoxide solution. The system is homogeneous and allows proton migration rates to be determined simply and reproducibly. Of considerable interest was the finding of a linear correlation between logarithms of the relative rates of base-catalyzed bromination of alicyclic ketones (I) and isomerization of methylenecycloalkanes (II).[1d] The suggestion of rate-determining allylic proton removal has been further substantiated by the observance of a large deuterium isotope effect.[2]

$$(CH_2)_{n-1}C=O \quad\quad (CH_2)_{n-1}C=CH_2$$
$$\text{I} \qquad\qquad\qquad \text{II}$$
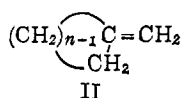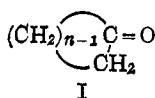
Variations in ring size from cyclobutyl to cyclooctyl in I and II lead to substantial rate differences, although these structures encompass small changes in inductive effects. Rate enhancements in small rings (cyclobutyl) were attributed to the proper geometry of the allylic C–H bond with respect to the π-orbitals of the unsaturated linkage in contrast to the unfavorable geometry of the allyl system in methylenecyclohexane.[1d]

It was of interest to determine the effect on rate of appropriate electron-withdrawing and -donating substituents in various positions of acyclic olefins and to demonstrate the direction and magnitude of their inductive and steric effects.

Results

The rate of base-catalyzed isomerization of 2-ethyl-1-butene (III) was compared with the rate of base-catalyzed bromination of 3-pentanone (IV). Plots of the log values of these two quantities fit on the same graph recently reported for the comparison of alkylidenecycloalkanes and cycloalkanones[1b] (Fig. 1). These results clearly establish similarities in the transition state

$$\text{III} \qquad\qquad\qquad \text{IV}$$

profiles of the cyclic–acyclic olefin isomerization reaction and the cyclic–acyclic ketone bromination reactions.

(1) (a) A. Schriesheim, J. E. Hofmann and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **83**, 3731 (1961); (b) A. Schriesheim and C. A. Rowe, Jr., *Tetrahedron Letters*, No. **10**, 405; (c) A. Schriesheim and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **84**, 3160 (1962); (d) A. Schriesheim, R. J. Muller and C. A. Rowe, Jr., *ibid.*, **85**, 3164 (1962).

(2) S. Bank, C. A. Rowe, Jr., and A. Schriesheim, *ibid.*, **85**, 2115 (1963).

The rates of isomerization of a number of terminal olefins of varying complexity are listed in Table I. All reactions were carried out in dimethyl sulfoxide–potassium *tert*-butoxide solutions at 55° with the exception of allylbenzene and 1,4-pentadiene. The latter two compounds isomerized at extraordinarily rapid rates and it was necessary to obtain their rates at 30° in a dimethyl sulfoxide–*tert*-butyl alcohol–potassium *tert*-butoxide solution.[1c] The rate constants were obtained from the slopes of first-order plots up to 30–50% conversion and are statistically corrected for reactable hydrogens. In addition, they have all been compared to 1-butene as the standard and are placed in order of descending rates. Where available, ΔE_{act}, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are listed. The 2-isomer predominates over the 1-isomer at equilibrium except in the case of 2,4,4-trimethyl-1-pentene where there is about 85% of the terminal olefin at equilibrium at 55°. Further reaction leading to other internal isomers are found when no structural limitations are present. However, these isomers are usually formed at a slow rate and do not complicate the rate studies.

Four basic olefin structures have been classified in the manner shown in Table II. Class I and II compounds are treated essentially as 3-substituted-1-propene and 3-substituted-2-methyl-1-propene derivatives, while class III and IV are 3-substituted-1-butene and 2-substituted-1-butene derivatives. The rates are listed relative to a methyl substituent in each class.

It was found that structural variation in the class I and II olefins gives rise to definite trends in reaction rates. Thus, as the substituents are varied from methyl to *tert*-butyl, the rate progressively decreases. The methyl-substituted compounds isomerize about 120–150 times faster than the *tert*-butyl substituted materials. Rate enhancements of a much greater magnitude result when electron-withdrawing groups such as phenyl or vinyl are present in series I olefins. Thus, allylbenzene and 1,4-pentadiene isomerize about 10^5 times faster than 1-butene. The effects of the various substituent groups upon the relative rates are therefore: vinyl $\cong$ phenyl $\gg$ methyl $>$ ethyl $\cong$ propyl $>$ isopropyl $>$ *tert*-butyl.

Class III and IV olefins give rise to the same trends within the scope of the substituents studied. Hydrogen substitution leads to a rate increase. In series III the hydrogen substituted material (1-butene) isomerizes 4.13 times faster than the methyl substituted compound 3-methyl-1-butene. The variation of substituent effect upon the rate is: hydrogen $>$ methyl $>$ ethyl $>$ isopropyl.