activated systems were used. Two substrates, malate and pyruvate, were employed to determine any effect of substrate upon the mechanism of quinone action. After the exposures, the systems were centrifuged and particulate and supernatant fractions were analyzed separately. If supernatant and particulate quinone pools do not equilibrate, isotopic exchange would appear only in the pool actively involved in oxidative phosphorylation, presumably the particulate fraction, and its detectability would be greatly enhanced by separate analysis.

The oxidative phosphorylation activity of the test systems is presented in Table I; the tritium incorporation into quinones recovered from the corresponding macro systems is shown in Table II.

All experiments displayed phosphate fixation coupled to oxidation both with malate and pyruvate. The tritium data indicate the lack of any significant isotope incorporation into the quinones. The extremely small residual activities are most likely due to traces of impurities since, particularly with native quinone, the quantities were small and there were accompanying highly radioactive lipoid fractions.[8] These could be a serious source of error if not completely removed and may explain the difference between our results and those reported.[3]

Lack of incorporation of tritium from T_2O into the quinone during oxidative phosphorylation indicates no carbon-hydrogen bond cleavage occurred in the quinone. Since this is a negative result, the possibility of undetected exchange must be considered. This might be possible if (a) there was a large isotope effect, and (b) only a small fraction of quinone was actively involved. However, the fact that the same results were obtained with particulate and supernatant fractions and exogenous and native quinones, and that the P_i fixed was large relative to the quinone present, argues against this assumption.

The best interpretation of our results is that the 2-methyl group is not directly involved, and therefore quinone methide mechanisms[2a-c] should be discounted. Complementary support for this conclusion is provided by similar experiments with 2-methyl-d_3-3-phytyl-1,4-naphthoquinone[9] in which we find that quinone recovered from reconstituted systems shows no loss of deuterium. The lack of incorporation of tritium also argues against involvement of the α-methylene hydrogens (as required in the fused furan mechanism[2a]) or the β-methine hydrogen. However, chromanol formation could occur without exchange because of the steric specificity of the β hydrogens in the pyran ring. The parallel experiments with phylloquinones-α-d_2[9] and -β-d are at hand.

(8) The quinone was extracted from the particulate and supernatant phases separately with 95% ethanol, and the ethanol extracts were diluted with an equal volume of saturated aqueous magnesium chloride solution and then extracted with pentane. The pentane extracts were repeatedly chromatographed on tlc-grade kiesel gel. Colorless bands both preceding and succeeding the quinone were highly radioactive.

(9) S. J. Di Mari, J. Supple, and H. Rapoport, *J. Am. Chem. Soc.*, 88, 1226 (1966).

(10) National Institutes of Health Predoctoral Fellow.

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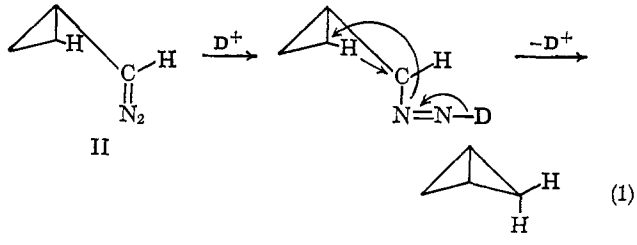
The Mechanisms of Base-Catalyzed Decomposition of Cyclopropanecarboxaldehyde *p*-Tosylhydrazone in Protic Solvents

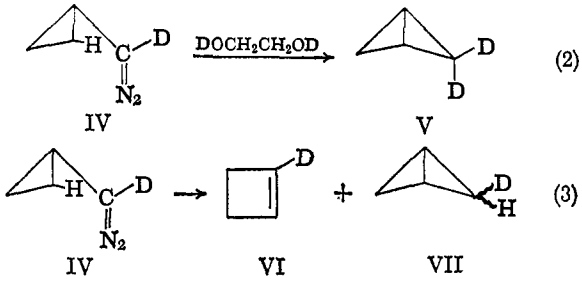
Sir:

Cyclopropanecarboxaldehyde *p*-tosylhydrazone (I) is decomposed by bases in aprotic solvents to cyclobutene, 1,3-butadiene, ethylene, and acetylene.[1] In protic environments, salts of I decompose primarily to bicyclo[1.1.0]butane and cyclobutene. It was suggested that salts of I thermolyze by carbenic processes involving cyclopropyldiazomethane, whereas in protic media the major path to bicyclo[1.1.0]butane involves cyclopropylmethyldiazonium or cyclopropylcarbonium intermediates. Recently[2] decomposition of I *in* ethylene glycol-d_2 by insufficient base was reported to yield bicyclo[1.1.0]butane which does *not* contain deuterium, and the following insertion mechanism was proposed (eq 1). Since these results and conclusions do not agree with present information, we shall summarize our studies of decomposition of salts of I in protic environments.



(1)

Decomposition of cyclopropanecarboxaldehyde-d_1 *p*-tosylhydrazone (III, Table I) in ethylene glycol-d_2 by insufficient, stoichiometric, or excess butyllithium gives bicyclo[1.1.0]butanes containing *two* (V, 77–87%) and *one* (VII, 12–19%) deuterium atoms, and cyclobutene essentially monodeuterated (VI, 93–98%). The *principal* process yielding bicyclo[1.1.0]butane results in incorporation of one deuterium from solvent to give V (eq 2); minor processes yield cyclobutene-d_1 (VI) and bicyclo[1.1.0]butane-d_1 (VII) without inclusion of external deuterium (eq 3).



(2)

(3)

Since reactions in excess base do not give appreciable quantities of dideuteriocyclobutene, neither III, nor its salt, nor IV undergoes significant deuterium exchange into the cyclopropane ring before decomposition. The near absence of trideuteriobicyclo[1.1.0]butane illustrates that deuterium exchange into bicyclo[1.1.0]-butanes is unimportant. Formation of cyclobutenes is enhanced upon effecting decompositions in excess base, in mixtures of protic and aprotic solvents, or in ethylene glycol-d_2 rather than protoethylene glycol.

(1) J. A. Smith, H. Shechter, J. Bayless, and L. Friedman, *J. Am. Chem. Soc.*, 87, 659 (1965).

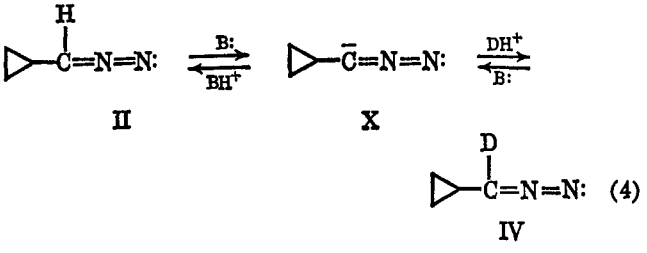
(2) K. B. Wiberg and J. M. Lavanish, *ibid.*, 88, 365 (1966).

Table I. Decomposition of Cyclopropanecarboxaldehyde-d_1 and Cyclopropanecarboxaldehyde *p*-Tosylhydrazones (III and I) in Ethylene Glycol-d_2

Butyllithium, moles × 10^{-3}	*p*-Tosylhydrazone, moles × 10^{-3}	Temp, °C	$DOCH_2$-CH_2OD, ml	% composition of principal products			Deuterium content, %						
													
	III						d_0	d_1	d_2	d_3	d_0	d_1	d_2
4.3	8.4	144	10	67	10		<1	17	77	<5			
4.1	4.2	143	5[a]	28	65	5	0	13	87	0	4	93	3
5.9	4.2	144	10	58	32	2	1	12	87	<1			
13.2	4.2	140	11.2	53	35	2	<1	19	78	3	2	98	<1
41.5	48.8	132	60[b]	76[c]	16	1	4	95	<1	<1	3	96	<1
	I												
4.2	8.2	132	10	70	12	1	15	75	10		95	4	1
40.3	50.4	139	60	77[d]	21	<1	24	74	2		96	4	≪1
42.0	42.0	137	20	63	34	2	11	74	15		85	15	<1
5.2	5.2	173	10	36	55	5	18	78	4		95	5	≪1
12.6	8.4	132	10	58	42		8	57	35		60	40	<1

[a] In Diethyl Carbitol (40 ml). [b] Reaction was effected in protoethylene glycol. [c] The nmr ratio of the *exo* and bridgehead hydrogens to *endo* hydrogens is 1.85:1. [d] The nmr ratio of the *exo* and bridgehead hydrogens to *endo* hydrogens is 2.9.

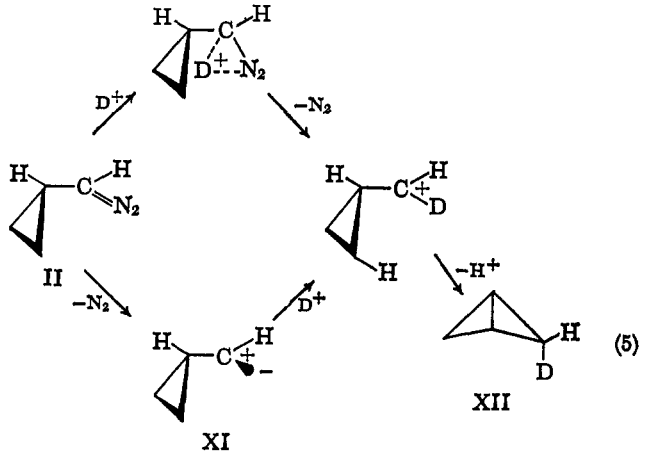
Decomposition of I in ethylene glycol-d_2 with insufficient butyllithium (0.2–0.8 equiv) yields bicyclo[1.1.0]-butanes containing *no* (VIII, 15–26%), *one* (VII, 69–78%), and *two* (V, 2–10%) deuteriums and cyclobutenes with *no* (IX, 94–95%) and *one* (VI, 4–5%) deuteriums. As the reaction temperatures or the equivalents of base are increased, the ratio of bicyclo-[1.1.0]butanes to cyclobutenes is diminished and there is less deuterium in the products. Upon increasing the equivalents of base further, the proportions of bicyclo-[1.1.0]butane containing *two* deuteriums (V, 8–35%) and cyclobutene containing *one* deuterium (VI, 5–40%) are significantly increased. A base-catalyzed process[2] (eq 4) thus occurs by which II yields IV which then gives products (eq 2 and 3).



II X IV (4)

The stereochemistry in conversion of I and III to monodeuteriobicyclo[1.1.0]butanes has been investigated. Reaction of I with butyllithium in ethylene glycol-d_2 gives bicyclo[1.1.0]butane-d_1 with 83–89% of its deuterium *endo*. Decomposition of III by butyllithium in protoethylene glycol yields bicyclo[1.1.0]-butane-d_1 with ~76% of its deuterium *exo*.[3] In formation of bicyclo[1.1.0]butane-d_1 by cationic decomposition of I or III, external protium or deuterium is introduced stereoselectively into the *endo* position.

Since bicyclo[1.1.0]butane is formed with *endo* incorporation of external protium, and cyclobutene and small quantities of bicyclo[1.1.0]butane are obtained without inclusion of solvent protons, several processes occur in transforming I to products in ethylene glycol. Bicyclo[1.1.0]butane resulting from stereoselective incorporation of external hydrogen cannot be derived from cyclopropylmethyldiazonium or cyclopropylcarbinyl cations in which there is complete rotation about the single bond connecting the cyclopropyl ring to its cationic substituent. The results are rationalizable if bicyclo[1.1.0]butane results from protonation of II or cyclopropylcarbinylene (XI) in specific conformations with (near) simultaneous cationic insertion in which stereochemistry is mostly maintained (eq 5).[4]



II XI XII (5)

Formation of cyclobutene without incorporation of external deuterium is interpretable by carbenic decomposition of II and IV (eq 3). That carbenic and cationic processes occur competitively in the proton donor environment is consistent with observations that formation of cyclobutene is favored upon effecting decompositions at elevated temperatures, in excess base, in solvents of limited proton–donor activity, and in ethylene glycol-d_2 rather than protoethylene glycol. This interpretation also agrees with observation that salts of I and III decompose in aprotic solvents to give cyclobutenes as major products.[1]

The bicyclo[1.1.0]butanes (8–26%) formed without deuterium incorporation in decomposition of I and III in ethylene glycol-d_2 remain for consideration. These products may arise in part from carbenic decomposition (eq 3) of II and IV; their proportions, however, as compared to cyclobutene, particularly when the reac-

(3) See ref 2.

(4) II and XI are represented as *cis*-bisected conformers; other conformations will give XII if deuteration and insertion are sufficiently rapid. *endo* protonation can also arise by intramolecular transfer of hydrogen coordinated at the under side of the cyclopropane ring of II.

tions are effected with insufficient base, are larger than experienced when the decompositions are effected in aprotic environments. It thus appears that minor cationic processes (eq 1) give bicyclo[1.1.0]butanes without incorporation of external label.

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On Twisted Arylethylene Dianions and Triplets

Sir:

Twisted structures (Figure 1) have been proposed for arylethylene dianions.[1] Aside from theoretical considerations, the best evidence for this has been that anion radicals of sterically strained arylethylenes (tetraphenylethylene, triphenylethylene) tend to disproportionate *via* electron transfer to a much greater extent than stilbene.[2] Disproportionation (eq 1)

$$2R_2\dot{C}-\bar{C}R_2 \rightleftharpoons R_2\bar{C}-\bar{C}R_2 + R_2C{=}CR_2 \qquad (1)$$

would be accompanied by relief of steric strain for each of the former pair of anion radicals, but not for the latter, if the dianions could readily assume twisted geometries but the anion radicals were constrained to seek planarity.

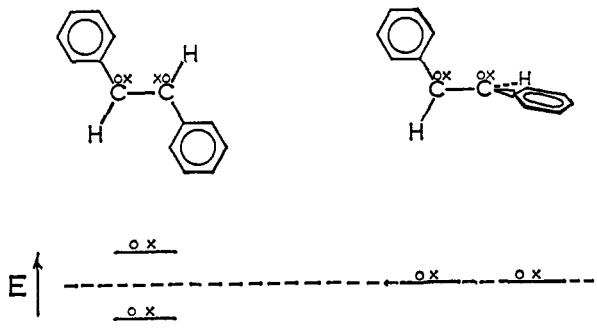

Figure 1. Partial HMO diagrams of stilbene triplets and dianions showing planar (left) and "perpendicular" (right) geometries. The circles represent electrons of the lowest energy $\pi-\pi^*$ triplet state. The circles and x's together represent electrons of the corresponding dianion. Only the two highest energy occupied orbitals are shown. The remainder of the electrons are identically described for both the triplet and the dianion in this theory. Since the orbital diagram is symmetric about $E = \alpha$ (dashed line), the net contribution of the depicted electrons is zero for both the triplet and the dianion at all angles of twist about the central carbon–carbon bond. Thus, identical twisting potentials are predicted by HMO theory for the two species.

Since there is another reasonable and obvious explanation for the same trend, the evidence cited above is ambiguous. The alternative explanation is that electron–electron repulsions are relatively greater in the stilbene dianion than in those of tri- and tetraphenylethylene even if these are all planar.[1a,3]

This ambiguity is not present in considerations of the data presented here.

A comparison of the disproportionation tendencies of stilbene and α-methylstilbene anion radicals shows that the latter are much more prone to disproportionate than the former. Representative data, together with some for tri- and tetraphenylethylene anion radicals, are presented in Table I.[4]

Table I. Disproportionation of Sodium Arylethylenes in 2-Methyltetrahydrofuran at 25°

Hydrocarbon	K^a
α-Methylstilbene	≥ 1000
Stilbene	0.09
Triphenylethylene	36
Tetraphenylethylene	≥ 1000

[a] K is the equilibrium constant for disproportionation of ion pairs to give a netural triple ion. The concentrations of ionic species ranged from *ca.* 10^{-5} to *ca.* 10^{-3} M. K is concentration independent through this range.

The effect of methyl substitution of stilbene is large. It is in the opposite direction from that which might be expected if a steric effect on the magnitude of the Coulombic interactions in the ionic aggregates were the important factor, since the dianion should be more sensitive to this kind of strain than the anion radical. It is difficult to view the large effect of methyl substitution as other than a steric effect reflecting a change in geometry accompanying disproportionation.[5]

Occasionally data from two different and independent areas of study are interrelated in such a way that each problem bears on the other. Such is the case for the problems of the geometries of arylethylene triplet states and the corresponding dianions.

Hammond and Saltiel were forced to postulate nonvertical energy transfer to *cis*-stilbene. They proposed the possibility that three varieties of the lowest lying $\pi-\pi^*$ triplet state of stilbene are metastable: *cis*,

(1) (a) N. S. Hush and J. Blackledge, *J. Chem. Phys.* 23, 514 (1955); (b) M. J. S. Dewar and P. Gray, Special Publication No. 12, The Chemical Society, London, 1958, pp 164–166; (c) J. F. Garst, E. R. Zabolotny, and R. S. Cole, *J. Am. Chem. Soc.*, 86, 2257 (1964); (d) R. C. Roberts and M. Szwarc, *ibid.*, 87, 5542 (1965).

(2) E. R. Zabolotny and J. F. Garst, *ibid.*, 86, 1645 (1964).

(3) Steric interactions would prevent complete planarity in the strained systems, but the calculations of ref 1a presume planarity.

(4) Data are presented for sodium counterion and 2-methyltetrahydrofuran solvent because under these conditions the formal equilibrium constant, K_F, for disproportionation is very nearly concentration independent in the range about 10^{-4} M for the systems for which it is measureable. K_F is computed from the concentrations of species measured without regard to state of ionic aggregation. The lack of concentration dependence of K_F indicates negligible dissociation of ion pairs, a factor which cannot be ignored in the more polar ethers (tetrahydrofuran and 1,2-dimethoxyethane).[1c,d] Under the experimental conditions of this report, the directly measured K_F can be taken as the equilibrium constant for the disproportionation of ion-pair anion radicals to give neutral triple ion dianion species. The same trend with hydrocarbon structure that is reported here is also observed for other counterion–solvent combinations.

The experimental methods employed here were the same as previously reported. The visible spectra of α-methylstilbene ions are nearly identical with those of the stilbene ions.[1c]

(5) The "twisting" discussed here is, of course, only one of several possible modes of change in geometry.