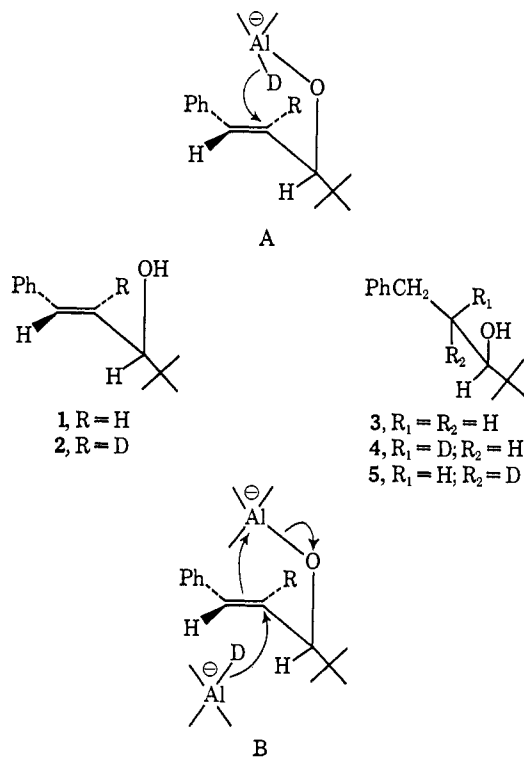


is not surprising in view of the fact that allyl alcohol is only partially reduced after heating for several hours with LAH in di-*n*-butyl ether at 100°. ⁵

So that the mildest possible conditions might be used for the reduction, the *t*-butyl group in the 3 position was replaced with a phenyl, which serves to activate the double bond to hydride attack. Models show that this substitution should not affect the conformational preference of the system. *trans*-1-*t*-Butyl-3-phenylallyl alcohol (**1**)⁶ was obtained as an oil in 98% yield by LAH reduction in refluxing THF of the propargylic alcohol produced by the reaction of lithium phenylacetylide with pivaldehyde.⁷ The ir (neat) showed conjugated C=C at 6.08 μ and *trans* CH at 10.80 μ ; nmr (CDCl₃) δ 0.95 (s, 9), 1.95 (s, 1), 3.85 (d, 1, *J* = 7 cps), 6.20 (q, 1, *J* = 7 and 15 cps), 6.58 (d, 1, *J* = 15 cps), and 7.3 (m, 5).

Reduction of this allylic alcohol by stirring with 2 moles of LAH in ether followed by hydrolysis of the intermediate, filtration of the alumina precipitate, and evaporation of the solvent gave a 98% yield of the saturated alcohol **3**, a clear oil; nmr (CDCl₃) δ 0.88 (s, 9), 1.5–2.0 (m, 3), 2.3–3.0 (m, 2), 3.2 (q, 1, *J* = 3 and 10 cps), and 7.24 (s, 5). The ABB' splitting of the methine proton by the adjacent methylene can be dissected using the preferred conformation of **3**, shown below with that for **1**. From the relationship of Karplus for the dependence of *J* on dihedral angle,⁸ the 10-cps coupling is assigned to H₁ and the 3-cps coupling to H₂.



Now, if the hydride donation is intramolecular and LAD is substituted for LAH, then compound **4** will be produced from **1** *via* transition state A. However, if it is intermolecular, **5** will be obtained *via* a transition

(5) F. A. Hochstein and W. G. Brown, *J. Am. Chem. Soc.*, **70**, 3484 (1948).

(6) All compounds gave satisfactory analytical data and a molecular ion whose exact mass was in agreement with the calculated value.

(7) E. E. Smisson, R. H. Johnson, A. W. Carlson, and B. F. Aycock, *J. Am. Chem. Soc.*, **78**, 3395 (1956).

(8) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

state which might resemble B. When the experiment was carried out, the nmr spectrum of the product showed the 10-cps coupling to have collapsed, demonstrating that **4** had been produced and that hydride attack is intramolecular. The other diastereomer, **5**, has also been obtained. When **2**, synthesized by the LAD reduction of 1-*t*-butyl-3-phenylpropargyl alcohol,⁷ was allowed to react with LAH in ether, the nmr of the product showed the expected doublet at δ 3.2, split by 10 cps with no trace of **4** detectable.

Work on the mechanism of the analogous reduction of propargylic alcohols is in progress, as is further application of the conformational preference of allylic systems such as **1** to other stereochemical problems.

Acknowledgment. The author wishes to thank John A. Katzenellenbogen and Professor E. J. Corey for stimulating discussions.

(9) National Science Foundation Predoctoral Fellow, 1965–1968.

Weston Thatcher Borden⁹

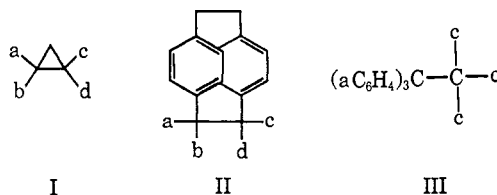
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Received January 13, 1968

Carbanion–Carbonium Ion Pairs as Intermediates in Racemization, Solvolyses, and Ring-Expansion Reactions¹

Sir:

Since ion pairs that involve carbonium ions² and carbanions³ are known to play prominent roles in isomerization and solvolytic reactions, it seemed probable that a system could be designed which upon heating in an appropriate solvent would produce a carbanion–carbonium ion pair from a covalent bond. The structural features envisioned as favoring such a transformation are as follows. (1) The covalent bond to be cleaved should be highly strained to provide a driving force for cleavage. (2) Carbanion-stabilizing substituents should be attached to one of the carbon atoms and carbonium ion stabilizing substituents to the second carbon atom involved in the cleavage. For example, systems I, II, and III all contain highly strained covalent carbon–carbon bonds which upon cleavage to an ion pair would release strain. Should substituents a and b be anion stabilizing, and c and d cation stabilizing, the covalent bond might undergo heterolysis when the systems are heated in polar solvents. These expectations have been realized in system IV.



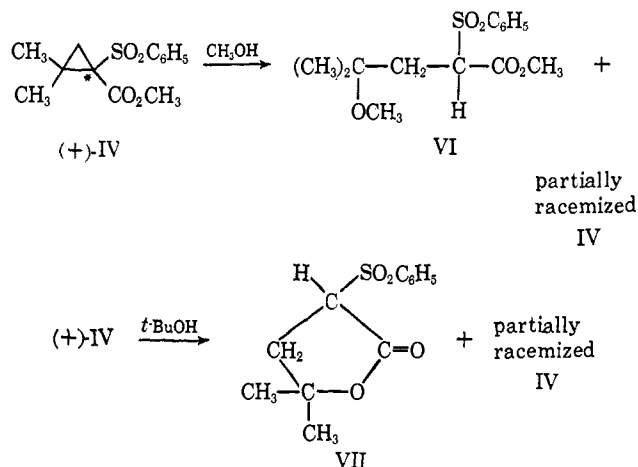
The substance was prepared in optically active form as follows. Metalation with *n*-butyllithium in ether of

(1) This investigation was supported in part by Public Health Service Research Grant No. GM 12640-02 from the Department of Health, Education, and Welfare.

(2) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(3) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965.

2,2-dimethyl-1-phenylsulfonylcyclopropane⁴ followed by carbonation gave derived acid V in 78% yield,⁵ mp 84–85° (from benzene). Acid V gave ester IV⁵ as a viscous oil in 95% yield when treated with diazomethane. Acid V was resolved through its quinine salt from ethanol, and the (+)-V⁵ obtained was brought to maximum rotation by fractional crystallization from benzene, mp 102–103°, $[\alpha]_{25}^{25,46} +20.7^\circ$ (*c* 5, chloroform), 25% yield. From filtrates of the quinine salt crystallization, (–)-V⁵ was recovered and brought to nearly maximum rotation by fractional crystallization from benzene, mp 100–102°, $[\alpha]_{25}^{25,46} -18.2^\circ$ (*c* 5, chloroform), 10% yield. Acid (+)-V (maximum rotation) gave (+)-IV⁵ as a viscous oil when treated with diazomethane in ether, $[\alpha]_{25}^{25,46} +17.9^\circ$ (*c* 2.3, chloroform).



Ester (+)-IV was heated in three solvents. In dimethyl sulfoxide after 6 hr at 125°, (+)-IV of maximum rotation gave IV with 85% recovery (purified by silica gel chromatography with ether–pentane as developer) which was 88% racemized. In methanol at 150° for 1.5 hr (+)-IV of maximum rotation gave IV, 15% racemized (37% recovery), and ether VI⁵ as an oil (55% yield), $[\alpha]_{25}^{25,46} -0.4^\circ$ (*c* 5, chloroform). The two compounds were separated by chromatography on silica gel with 20% ether–80% pentane as developer. In *t*-butyl alcohol at 150° for 17 hr (+)-IV of maximum rotation gave IV which was 43% racemized (67% recovery), isobutylene, and lactone VII⁵ (5%), mp 97–98°, $[\alpha]_{25}^{25,46} -0.50^\circ$ (*c* 5, chloroform). Again the products were isolated by chromatography on silica gel with an ether–pentane developer. The above compounds were also identified by their nmr and ir spectra, which were consistent with expectations. In all runs, olefins were also produced (nmr evidence), but these were not isolated and characterized.

To reduce the yield data to values which can be used for preliminary comparisons, one-point first-order rate constants were calculated for the racemization reactions in all three solvents and for the solvolysis reactions in methanol and *t*-butyl alcohol. In these calculations it was assumed that all product not recovered as IV had undergone solvolysis, and that the reactions were first order in starting material. The possibility of the order being other than first order is remote. Table I records the results.

(4) A. Ratajczak, F. A. L. Anet, and D. J. Cram, *J. Am. Chem. Soc.*, **89**, 2072 (1967).

(5) All new compounds reported here gave carbon and hydrogen analyses within 0.2% of theory.

Table I. Crude One-Point Rate Constants for Racemization and Solvolysis of (+)-IV

Solvent	Temp, °C	k_r , ^a sec ⁻¹ , × 10 ⁵	k_s , ^b sec ⁻¹ , × 10 ⁵	$k_r + k_s$, sec ⁻¹ , × 10 ⁵	k_s/k_r
(CH ₃) ₂ SO	125	9.7		9.7	
CH ₃ OH	150	2.1	18	20	9
(CH ₃) ₂ COH	150	0.92	0.66	1.6	0.7

^a First-order rate constant for racemization. ^b First-order rate constant for solvolysis, based on recovery of starting material.

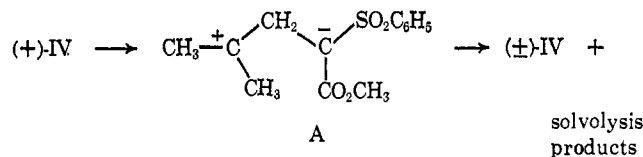
These results support the notion that the reactions in question occur through carbonium ion–carbanion ion pair intermediates. Clearly, racemization cannot occur without covalent bond cleavage, reorganization of the intermediate produced, and collapse to the covalent state. The cleavage must be either heterolytic or homolytic. Three pieces of evidence point to heterolytic cleavage. (1) The open-chain products VI and VII are of the type that arise from ions, not radicals, and the chances are high that both the solvolytic and the racemization reactions involve common intermediates. (2) The pattern of reactivity variation with solvent resembles that of solvolytic reactions, and not of radical reactions. Although crude, the rate constants of Table I differ enough to make the general pattern visible. If $k_r + k_s$ (sum of rate constants for racemization and solvolysis) is used as a gross measure of ionization rate,⁶ methyl alcohol provides a rate greater by a power of ten over that in *t*-butyl alcohol. In solvolysis of *t*-butyl chloride, methanol produces a rate faster by about two powers of ten than *t*-butyl alcohol as solvent.^{7a} The observed rate difference for IV in the two solvents is greater than that expected for a radical cleavage. If the difference in temperature is taken into consideration, the rates for IV in methanol and dimethyl sulfoxide are of the same order of magnitude, with dimethyl sulfoxide providing the faster rate. Others have found ionization rates of tosylates to differ by a factor of about eight (favoring methanol) in these two solvents.^{7b} (3) The ratio k_s/k_r is over ten times as great in methanol as in *t*-butyl alcohol. This type of relationship is expected on the basis of an ion-pair mechanism since methanol is both more acidic and more nucleophilic than *t*-butyl alcohol.

The possibility exists that in the ionization of starting material covalent carbon–oxygen bonds are made to give oxonium–carbanion ion pairs. Although some of the product might arise by such a path, it is likely that most of it went through the carbonium–carbanion ion-pair intermediate, particularly in view of the fact that the carbonium ion is tertiary and that racemization was competitive with solvolysis, even in methanol.

Thus, the evidence points to ion-pair A as a discrete intermediate in the reactions. It is interesting that solvolysis products VI and VII exhibit rotations so low as to suggest that they are racemates. Thus, the carbanion portion of A underwent a symmetrizing operation before going to product, a property formerly ob-

(6) These values are minimal since the ionization rate constant is the sum of k_r , k_s , and a rate constant for that part of the ionization which returns to starting material of unchanged configuration (invisible reaction).

(7) (a) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956); (b) S. G. Smith, A. H. Fainberg, and S. Winstein, *ibid.*, **83**, 618 (1961).



served characteristic of carbanions stabilized by ester groups^{8a} but not by sulfone groups.^{8b}

A large number of novel reactions can be envisioned which are based on the carbonium ion-carbanion ion pair concept and generalized systems such as I, II, and III. Molecular rearrangements of the allylic variety, ring enlargements, epimerizations, racemizations, additions to polarized double bonds, solvolyses, and eliminations are all anticipated. A survey of these possibilities is actively being pursued.

(8) (a) D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfeld, *J. Am. Chem. Soc.*, **83**, 3678 (1961); (b) D. J. Cram, W. D. Nielsen, and B. Rickborn, *ibid.*, **82**, 6415 (1960).

(9) Fulbright Visiting Scholar at University of California at Los Angeles from The Institute of Technology (Politechnika), Lodz, Poland.

Donald J. Cram, Aleksander Ratajczak⁹

Contribution No. 2070, Department of Chemistry
University of California at Los Angeles, Los Angeles, California

Received February 7, 1968

Formation of Cyclopropanes via the Photosensitized Decomposition of Aliphatic α -Diazo Ketones¹

Sir:

Intramolecular reactions of carbenes very often dominate intermolecular ones. Typical of this general problem is the inability to avoid the photochemical Wolff rearrangement^{2,3} on irradiation of aliphatic α -diazo ketones.⁴ It seemed to us that triplet intermediates should find intramolecular pathways more difficult than do their singlet counterparts, and might well be trapped by intermolecular agents.

This communication reports some examples in which the photochemical Wolff rearrangement can be avoided or diminished by employing benzophenone as a sensitizing agent. Irradiation of an olefinic solution of diazocyclohexanone with two GE Sunlamps followed by addition of methanol led to moderate yields of the Wolff product, I. When benzophenone was added to the solutions I was replaced in 17–40% yield with the spiro ketones produced, at least formally, by addition of the ketocarbene to the host olefin. Of the few examples known of cyclopropane formation on irradiation of α -diazo ketones, the best studied involves benzoylcarbene. Cyclopropanes are formed in both the sensitized and unsensitized decompositions, indicating rapid intersystem crossing in this aromatic system.⁵ Increased hydrogen abstraction in polar media has also been found in the sensitized reaction.⁶

(1) This work was supported by the National Science Foundation (Grants GP-5257 and GP-7819). Additional thanks are due for generous help in purchasing a Varian Associates HA-100 nmr spectrometer through Grant GP-5200.

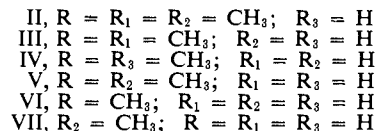
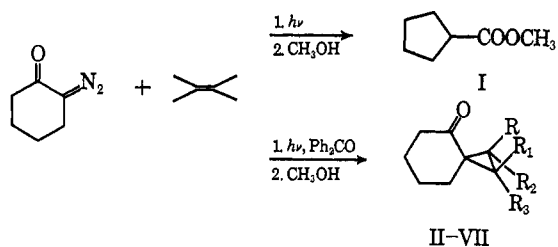
(2) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 115 ff.

(3) F. Weygand and H. J. Bestmann, *Angew. Chem.*, **72**, 535 (1960).

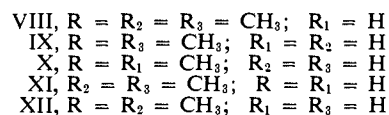
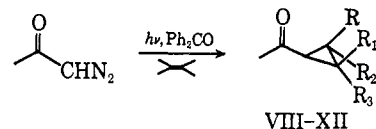
(4) An exception seems to be the carbene derived from ethyl trifluoroacetyl diazoacetate: F. Weygand, W. Schwenke, and H. J. Bestmann, *ibid.*, **73**, 409 (1961).

(5) D. O. Cowan, M. M. Couch, K. R. Kopecky, and G. S. Hammond, *J. Org. Chem.*, **29**, 1922 (1964).

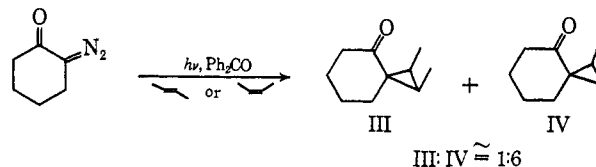
(6) A. Padwa and R. Layton, *Tetrahedron Letters*, 2167 (1965).



The sensitized decomposition of diazoacetone in olefins yields similar adducts in comparable yields. No adducts could be found in the unsensitized reactions.



The gross structures of the adducts are determined by independent synthesis (X–XII), comparison of spectra with those of authentic samples (VI, VII, XII),^{7–9} and spectral analysis of all. Details of the stereochemistry of the adducts are also settled. The sensitized decomposition of diazocyclohexanone in either *cis*- or *trans*-2-butene leads to the same mixture of cyclopropanes.¹⁰ The *trans* relation of the methyl groups in IV can be determined from the nmr spectrum which shows two different methyl signals. The structure of III is determined in the following manner: a chemical shift of *ca.* 0.2 ppm is observed between methyl groups *syn* and *anti* to the carbonyl [nmr (ppm): II, 8.95 (1), 9.12 (2); III, 9.07; IV, 8.95 (1), 9.10 (1); V, 8.78 (1), 9.06 (1); VI, 9.07; VII, 8.88]. It remains only to determine which set belongs to *syn* methyls and which to *anti*. Of the two products of addition to propylene, VI and



VII, only VI is rearranged to allylcyclohexanone on heating to 250° and therefore must have the *syn* structure.⁹ As VI has its methyl signal at high field, it is the high-field group of signals which belongs to the *syn* methyl groups and the low-field group which belongs to the *anti* methyl groups. On this basis III must have the *syn* structure. Similarly, II has two methyl groups *syn* and one *anti*. The absence of the *anti,cis* isomer is

(7) We thank Professor William G. Dauben⁸ for providing infrared spectra of VI and VII and Professor Royston Roberts⁹ for the infrared spectrum of XII.

(8) W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, **89**, 3449 (1967).

(9) R. M. Roberts and R. G. Landolt, *ibid.*, **87**, 2281 (1965).

(10) Control experiments show that these ketones are only very slowly isomerized under the reaction conditions.