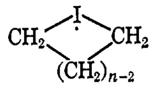
"Classical" Behavior of 4-Iodobutyl Radicals Generated in the Reaction of 1,4-Diiodobutane with Sodium Naphthalene

Sir:

Recent reports have included suggestions that 3-iodopropyl, 4-iodobutyl, and 5-iodopentyl radicals may be bridged (**1**) or may undergo unusual reactions, such as internal S_H displacements at carbon (eq 1).[1-3]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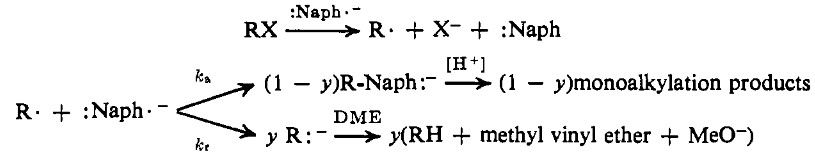
$$I(CH_2)_{n-1}CH_2\cdot \longrightarrow c\text{-}(CH_2)_n + I\cdot \qquad (1)$$

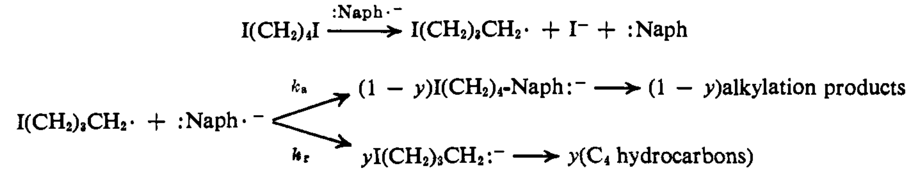
Because both possibilities are otherwise undocumented, and because their substantiation would have important structural and mechanistic consequences, we have tested their applicability to 4-iodobutyl radicals generated in the reactions of 1,4-diiodobutane with sodium naphthalene.

Scheme I[a]



[a] Sodium counterions are omitted.

Scheme II[a]



[a] Sodium counterions are omitted.

We find no evidence of bridging or of internal S_H reactions at carbon. In fact, 4-iodobutyl radicals generated in this reaction behave as would be expected of any unsubstituted primary alkyl radicals produced under the same conditions.

There is ample evidence that the mechanism of Scheme I applies to reactions of simple primary alkyl halides, including iodides, when the alkyl halides are dilute and sodium naphthalene is in excess in DME at 25°.[4,5] In Scheme I, y is the number of moles of alkylsodium (R:⁻) produced from 1 mole of alkyl halide (RX). It is related to the ratio of rate constants, k_a/k_r, as follows: $k_a/k_r = y/(1 - y)$. For simple primary alkyl halides $y = 0.53 \pm 0.05$, corresponding to $k_a/k_r = 0.9 \pm 0.2$.[6]

Application of Scheme I to the reaction of 1,4-diiodobutane generates Scheme II, in which 4-iodobutylsodium and alkylation products arise in competitive reactions analogous to those of Scheme I. Although 4-iodobutylsodium is expected to undergo other reactions, in addition to its possible reactions with solvent, all of these must lead to C_4 hydrocarbons. Thus, y(1,4-diiodobutane) can be calculated from the total amount of C_4 hydrocarbons formed.

If k_a/k_r were identical for 4-iodobutyl radicals and other primary alkyl radicals, namely, 0.9 ± 0.2, then y(1,4-diiodobutane) would be 0.53 ± 0.05. In order to test this prediction, "evaporation" experiments[5] with 1,4-diiodobutane were performed.

As expected, there were no C_8 hydrocarbons among the products. The C_4 hydrocarbons consisted only of cyclobutane (0.53, 0.49, and 0.50 mole per mole of 1,4-diiodobutane). No methyl vinyl ether was formed. The only other products, besides naphthalene and sodium iodide, were alkylation products.[8] Thus,

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(1) L. Kaplan, *J. Amer. Chem. Soc.*, **89**, 1753, 4566 (1967); *Chem. Commun.*, 754 (1968). The first of these papers reports cyclopropane and cyclopentane formation in decompositions of peroxides in benzene solutions of 1,3-diiodopropane and 1,5-diiodopentane, respectively. It is assumed that the cycloalkanes arise in unusual reactions of intermediate iodoalkyl radicals.

(2) P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **91**, 582 (1969). Bridging (**1**) in the 4-iodobutyl radical is suggested.

(3) Bridging in a 4-bromoalkyl radical has been suggested by M. P. Cava, M. Krieger, P. Pohlke, and D. Mangold, *ibid.*, **88**, 2615 (1966).

(4) (a) J. F. Garst, J. T. Barbas, and F. E. Barton, II, *ibid.*, **90**, 7159 (1968). See also (b) G. D. Sargent and G. A. Lux, *ibid.*, **90**, 7160 (1968).

(5) The reactions of alkyl iodides with sodium naphthalenide are so fast that it is difficult to achieve reactions in which RI is dilute, :Naph·⁻ is relatively concentrated, and the solutions are homogeneous in concentration and temperature throughout the duration of the reactions. This was accomplished in ref 4a and in the present work by slowly "evaporating" the alkyl iodide into a stirred, concentrated (*ca.* 0.1 *M*) solution of sodium naphthalene in DME at 25°. We refer to these as "evaporation" experiments.

(6) The error limits represent the judgment of the authors. They are nearly the extreme variation encountered. Data from ref 4a, for 5-hexenyl radicals, and from ref 7, for cyclopentylmethyl radicals, were considered, some experiments being given more weight than others. In addition, the data of ref 4b, for pentyl radicals, can be made consistent with this figure.

(7) J. F. Garst and F. E. Barton, II, *Tetrahedron Lett.*, 587 (1969).

(8) Reactions were carried out as previously described.[5] Yields were calculated from vpc measurements, using internal standards and flame-ionization detection. Products stated to be absent produced new peaks in vpc traces of reaction mixtures when authentic samples were added. This test was not applied to C_4 hydrocarbons, however. There was but one peak in the C_4 hydrocarbon region. The material producing it was trapped, using a splitter to divert 90% of the gas stream from the detector. It gave a single nmr peak in CCl_4 at τ 8.03.[9] When the material of this vpc peak was led into a Hitachi RMU6 mass spectrometer, the resulting spectrum matched in detail that reported for cyclobutane,[10] with no impurity peaks not attributable to background. Vpc peaks at longer retention times than naphthalene are ascribed to akylation products. These have been described in detail by Lipkin, Divis, and Jordan, as they obtained them from the reaction of 1,4-dichlorobutane with sodium naphthalene.[11] We have carried out this reaction, as well as that of 1,4-dibromobutane, with sodium naphthalene. The vpc traces of both these reactions match those from the 1,4-diiodobutane reactions. When all three reaction mixtures are mixed, no new shoulders or peaks appear in the vpc trace for the region of alkylation products, or, for that matter, any other portion of the vpc trace. Further, the three "alkylation" vpc peaks correspond to materials with the expected parent ions in their mass spectra, *m/e* 184, corresponding to $C_{14}H_{16}$.

(9) Identical with the value tabulated by J. R. Dyer, "Applications

y(1,4-diiodobutane) = 0.51 ± 0.02, in quantitative agreement with the prediction that 4-iodobutyl radicals behave "classically," *i.e.*, like unsubstituted primary alkyl radicals, in this system.

Not only are unusual structures and reactions like those previously suggested not *required* to account for these results, they are contraindicated. If the 4-iodobutyl radicals were bridged, k_a/k_r equal to that for simple primary alkyl radicals would have been unexpected, since this ratio apparently reflects electronic factors.[12] Similarly, if the 4-iodobutyl radicals were generating cyclobutane through internal S_H reactions, y should have been greater than that predicted on the basis of the assumption that this is not occurring. Thus, we conclude that it is unlikely that the 4-iodobutyl radicals generated in the present experiments have bridged structures, undergo internal S_H reactions, or behave in any other "nonclassical" fashion.[13,14]

The origin of the cyclobutane in the present experiments deserves comment. It clearly arises in unimolecular reactions of 4-iodobutylsodium. The mechanism of this reaction will be considered elsewhere.

Acknowledgment. This work was supported by a grant from the National Science Foundation. We thank Professor L. Kaplan for permission to quote unpublished results.

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of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 86.

(10) "Mass Spectral Data," compiled by the American Petroleum Institute, Research Project 44, Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

(11) D. Lipkin, G. J. Divis, and R. W. Jordan, *Preprints, Div. Petrol. Chem.*, 13, D60 (1968).

(12) Thus, k_a/k_r increases from simple primary to simple secondary and tertiary free radicals, an effect believed to be due to electronic factors.[4b]

(13) (a) Chock and Halpern report no cyclobutane from the reactions of 1,4-diiodobutane with $Co(CN)_5^{3-}$.[2] 4-Iodobutyl radicals are believed to be intermediates. Clearly they do not undergo internal S_H reactions. Although the reactions of 1,3-diiodopropane with $Co(CN)_5^{3-}$ gave cyclopropane, these authors prefer a mechanism for its formation not involving an internal S_H reaction. (b) Professor L. Kaplan has recently informed us that 1,4-diiodobutane does not give cyclobutane under the reaction conditions described in ref 1. Experiments in our laboratories are in agreement with this result.

(14) For reactions of sodium anthracene with simple alkyl halides in DME, y is very small (*ca.* 0.03 or less). Similarly, sodium anthracene reacts with 1,4-diiodobutane to produce only about 0.03 mole of cyclobutane per mole of alkyl iodide. This supports our conclusions by providing another system for which the behavior of primary alkyl halides and 1,4-diiodobutane are parallel. The same seems to be true for reactions of sodium biphenyl.

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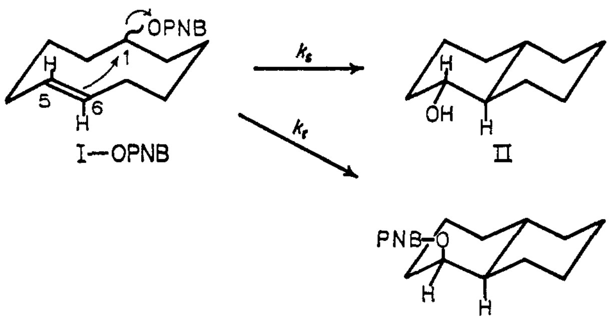
On the Chemistry and Stereochemistry of the Ion Pair Derived from *trans*-5-Cyclodecen-1-yl *p*-Nitrobenzoate.[1]

Sir:

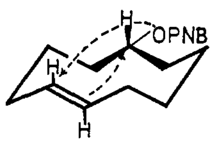
We wish to report an ion-pair rearrangement in which a *p*-nitrobenzoate ion migrates a considerable distance with incomplete randomization of the carboxyl oxygen atoms.

In an earlier investigation[2] it was found that solvolysis of *trans*-5-cyclodecen-1-yl *p*-nitrobenzoate (I-OPNB) in aqueous acetone gives *trans,trans*-1-decalol (II) and is accompanied by isomeric rearrangement to *trans,cis*-1-decalyl *p*-nitrobenzoate (III). Both transformations are first order and the rearrangement is intramolecular (no exchange with *p*-nitrobenzoate ion). It was also observed that rearrangement of I-OPNB-carbonyl-^{18}O results in only partial equilibration of the oxygen atoms.[2]

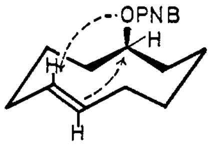
From the high reactivity (I-OPNB is > 10^4 times more reactive than cyclodecyl *p*-nitrobenzoate)[2] it is clear that solvolysis is accelerated by transannular participation by the double bond. The effect of varying solvent and temperature on the rates of solvolysis (k_s) and rearrangement (k_r) and on the k_s/k_r ratio indicates that assisted ionization gives rise to an ion-pair intermediate which is common to solvolysis and rearrangement, *i.e.*, rearrangement results from ion-pair return.



The migration distance of the *p*-nitrobenzoate ion in the rearrangement depends on the stereochemistry of the ionization step. Assisted ionization with inversion of C_1 (IV) accounts for the rate enhancement and stereochemistry of solvolysis (*trans* addition of C_1 and solvent to the double bond). In this case the anion is generated a considerable distance from C_5. On the other hand, a process involving retention of configuration at C_1 (V) requires a much shorter migration route and provides an obvious explanation for the stereochemistry of rearrangement (*cis* addition to the double bond)[3] if not for incomplete scrambling of oxygen atoms.



IV



V

We have now determined the relative configurations of C_1 in the reactant (I-OPNB) and products (II and III) and have established that ionization results in inversion of C_1 as in IV. We have also reinvestigated oxygen equilibration associated with rearrangement and have confirmed that equilibration is incomplete.

The *trans*-5-cyclodecen-1-yl system (I) was resolved by recrystallization of the cinchonidine salt of the acid phthalate derivative and the absolute configuration of active I was determined by correlation with β-methoxyadipic acid.[4,5] (+)-*trans*-5-Cyclodecen-1-ol (I-

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(1) Supported by the National Institutes of Health (GM-14134) and the Directorate of Chemical Sciences, Air Force Office of Scientific Research (AFOSR-847-67).

(2) H. L. Goering and W. D. Closson, *J. Am. Chem. Soc.*, 83, 3511 (1961).

(3) *Cf.* M. J. S. Dewar and R. C. Fahey, *ibid.*, 85, 2245, 3645 (1963).

(4) M. Viscontini and P. Miglioretto, *Helv. Chim. Acta*, 38, 930 (1955); K. Brenneisen, Ch. Tamm, and T. Reichstein, *ibid.*, 39, 1233 (1956).