

$\gamma(1,4\text{-diiodobutane}) = 0.51 \pm 0.02$, 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 SH reactions, γ 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 SH 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.

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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 $\text{Co}(\text{CN})_5^{3-}$.² 4-Iodobutyl radicals are believed to be intermediates. Clearly they do not undergo internal SH reactions. Although the reactions of 1,3-diiodopropane with $\text{Co}(\text{CN})_5^{3-}$ gave cyclopropane, these authors prefer a mechanism for its formation not involving an internal SH 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, γ 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.

John F. Garst, John T. Barbas

Department of Chemistry, The University of Georgia
Athens, Georgia 30601

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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.

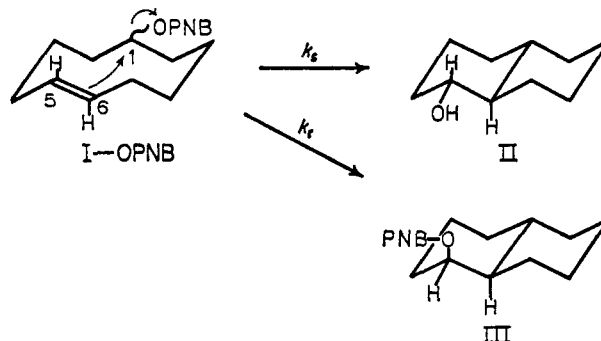
In an earlier investigation² it was found that solvolysis

(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).

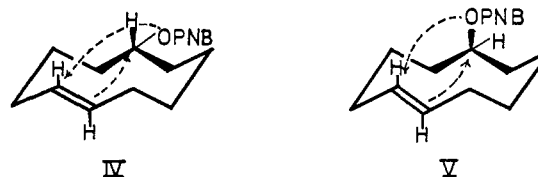
(2) H. L. Goering and W. D. Closson, *J. Am. Chem. Soc.*, 83, 3511 (1961).

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-¹⁸O 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.



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-

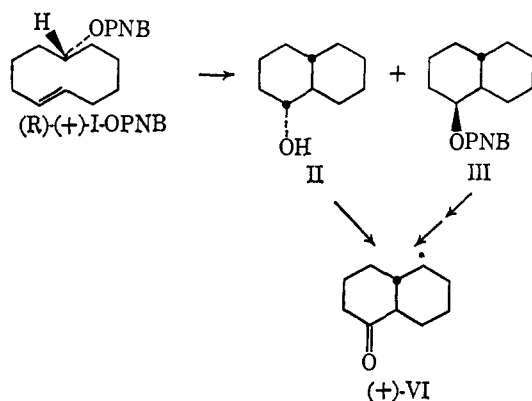
(3) Cf. M. J. S. Dewar and R. C. Fahey, *ibid.*, 85, 2245, 3645 (1963).

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

OH), $[\alpha]_{365}^{20}$ 21.1° (*c* 1.6, CHCl₃), was converted⁶ to (+)-I-OCH₃, $[\alpha]_{365}^{20}$ 24.2° (*c* 0.9, CHCl₃). Cleavage⁷ of the double bond followed by esterification of the diacid gave (-)-dimethyl 5-methoxysebecate, $[\alpha]_{365}^{20}$ -0.90° (*c* 3.56, CHCl₃).⁵ This acid was shown to have the *R* configuration by comparison with (S)-(+)-dimethyl 5-methoxysebecate, $[\alpha]_{365}^{20}$ 2.85° (*c* 3.02, CHCl₃), derived from (S)-(-)-β-methoxyadipic acid, $[\alpha]_{365}^{20}$ -23.8° (*c* 6.03, CHCl₃),^{4,8} as follows. Optically active (S)-(-)-β-methoxyadipic acid⁸ was converted to (S)-(+)-3-methoxy-1,6-hexanediol by reduction with LiAlH₄. The active methoxyglycol was converted to the ditosylate which was added to a DMF solution of 2 equiv of sodium diethylmalonate. Saponification and decarboxylation followed by esterification gave (S)-(+)-dimethyl 5-methoxysebecate. These correlations show that (+)-I-OH, and the related (+)-I-OPNB, have the *R* configuration.

The absolute configurations of II and III derived from active I-OPNB were established by conversion to active *trans*-α-decalone of known configuration.⁹

Solvolytic of (*R*)-(+)-I-OPNB in 90% acetone at 100° gave active II and III which were separately converted to (+)-*trans*-α-decalone (VI) (both samples showed a negative Cotton effect in methanol).⁹ In a parallel experiment it was found that (-)-*trans*-α-decalone (positive Cotton effect in methanol) is derived from (S)-(-)-I-OPNB. This establishes that cyclization of I-OPNB involves inversion of C₁ as in IV. Thus, the *p*-nitrobenzoate ion migrates a considerable distance in the I → III rearrangement. The observed stereoselectivity may result from the fact that return to the *trans,trans* isomer (II-OPNB) requires an even longer migration route and therefore does not compete with solvent capture.



The results of the ¹⁸O experiments are summarized in Table I. In these experiments ether- and carbonyl-¹⁸O-labeled I-OPNB was solvolyzed and the distribution of the label in the rearrangement product (III) was determined^{2,10}—scrambling does not occur prior or subsequent to the rearrangement and no label is lost.² Carbonyl-labeled ester was described earlier;² ether-

(5) Satisfactory elemental analyses were obtained for all new compounds, and ir and nmr spectra of active compounds were indistinguishable from those of authentic racemic samples.

(6) M. Neeman, M. C. Caserio, J. D. Roberts, and W. S. Johnson, *Tetrahedron*, **6**, 36 (1959).

(7) V. Prelog, H. J. Urech, A. A. Bothner-By, and J. Würsch, *Helv. Chim. Acta.*, **38**, 1095 (1955).

(8) A. Lardon and T. Reichstein, *ibid.*, **32**, 1613 (1949).

(9) C. Djerassi and J. Staunton, *J. Am. Chem. Soc.*, **83**, 736 (1961).

(10) H. L. Goering and J. F. Levy, *ibid.*, **84**, 3853 (1962).

Table I. Carboxyl Oxygen Equilibration for the I-OPNB → III Rearrangement in 90% Acetone at 100°

| Labeled I-OPNB (amt) ^a | Amt ^a of ether- ¹⁸ O for III | % equilibration |
|--|--|---------------------|
| Ether- ¹⁸ O (3.95 ± 0.04) ^b | 2.57 ± 0.01 ^b | 70 ± 1 ^b |
| Ether- ¹⁸ O (3.95 ± 0.04) | 2.54 ± 0.02 | 71 ± 2 |
| Carbonyl- ¹⁸ O (2.47 ± 0.01) | 0.90 ± 0.01 | 73 ± 1 |
| Carbonyl- ¹⁸ O (3.98 ± 0.04) ^c | 1.35 ± 0.02 | 69 ± 2 |

^a Atom % excess ¹⁸O. ^b Uncertainties determined from limiting values for a series of determinations. ^c Data in this row taken from ref 2.

labeled ester was prepared from *trans*-5-cyclodecenone-¹⁸O (LiAlH₄ reduction followed by esterification) which was obtained by base-catalyzed exchange of the ketone¹¹ and H₂¹⁸O in dioxane.

The ¹⁸O experiments confirm that rearrangement does not result in complete oxygen equilibration. This is a remarkable result considering the long migration route (IV) and points up a most interesting property of the ion-pair intermediate(s) involved in this transformation. Evidently the carboxyl oxygen atoms are not equivalent in ion pairs related to unreactive secondary alkyl esters. In some ways the present result is similar to the report¹² that the α-phenylethyl α-naphthoate ion pair gives ester with both inversion and retention of configuration with incomplete (~60%) oxygen equilibration. The required relocation of the ions for forming inverted product appears to be similar to that involved in the I → III rearrangement.

(11) P. S. Wharton, G. A. Hiegel, and R. V. Coombs, *J. Org. Chem.*, **28**, 3217 (1963); E. M. Kosower, W. D. Closson, H. L. Goering, and J. C. Gross, *J. Am. Chem. Soc.*, **83**, 2013 (1961).

(12) E. H. White and D. J. Woodcock, "Chemistry of the Amine Group," S. Patai, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968, p 450.

Harlan L. Goering, Robert F. Myers

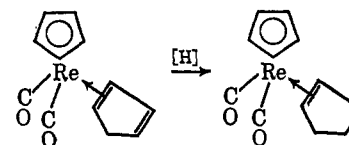
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

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Stereospecific Hydrogenation of Nickelocene¹

Sir:

Organometallic complexes containing partially coordinated ligands have often been hydrogenated and the amount of hydrogen consumed taken as a measure of the extent of uncoordinated unsaturation in the ligands, *e.g.*²



Analogous examples have been reported for complexes of iron,³ chromium,³ cobalt,⁴ and molybdenum.⁵ Nickelocene, (π-C₅H₅)₂Ni, is similarly hydrogenated

(1) Presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 13-18, 1969.

(2) M. L. H. Green and G. Wilkinson, *J. Chem. Soc.*, 4314 (1958).

(3) E. O. Fischer and J. Müller, *J. Organometal. Chem.*, **1**, 464 (1964).

(4) A. Nakamura and N. Hagihara, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **82**, 1392 (1961); see *Chem. Abstr.*, **59**, 2855h (1963).

(5) R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 4557 (1960).