(24) Another nitrogen-centered free radical that reacts with benzene is the N-succinimidyl radical;[25] Hedaya et al. showed that this radical most probably has a σ-type electronic ground state.[16a]

(25) D. R. Howton, *J. Am. Chem. Soc.*, **69**, 2060 (1947).

(26) When a frozen solution of **5a** in methylcyclohexane (77 K) was irradiated in the cavity of an ESR apparatus, only signals of methyl radicals and (probably) *t*-BuOO · radicals were observed.

(27) B. J. Hunt and W. Rigby, *Chem. Ind. (London)*, 1868 (1967).

(28) J. D. Kendall and G. F. Duffin, British Patent 797,144 (1958); *Chem. Abstr.*, **53**, 4983 (1959).

(29) Very recently, the synthesis of 1-pyrazolecarbonyl chloride has also been described by Peterson et al.;[30] these authors reported mp 52–54°, and pointed out the extremely lachrymatory character of this compound, a property also observed by us.

(30) L. K. Peterson, E. Kiehlmann, A. R. Sanger, and K. I. Thê, *Can. J. Chem.*, **52**, 2367 (1974).

Ion-Pair Return Associated with Solvolysis of 1,2-Dimethyl-*exo*-2-norbornyl *p*-Nitrobenzoate-$^{18}O^1$

Harlan L. Goering* and Krešimir Humski

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, and Faculty of Technology, University of Zagreb, 44000 Sisak, Croatia, Yugoslavia
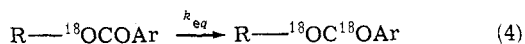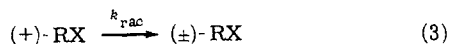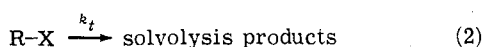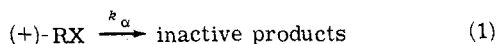
Solvolysis of 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate (I-OPNB) in 90% aqueous acetone involves exclusive alkyl–oxygen cleavage and is accompanied by ion-pair return which results in racemization of optically active I-OPNB and randomization of the carboxyl oxygen atoms of ^{18}O-labeled I-OPNB. In this system the carbonium ion is not symmetrical and k_{rac} corresponds to an upper limit of 37% of the total return from product-forming intermediates. The relative rates of racemization and carboxyl oxygen equilibration indicate that k_{eq} corresponds to ~20% of the total return.

Several methods for detecting ion-pair return associated with SN1 solvolytic reactions have been reported. These include salt effects,[2,3] isomerization of the cation[2b,4,5] or anion,[6] racemization of the unsolvolyzed substrate,[2b,5,7] randomization of carboxyl or sulfoxyl oxygen atoms,[5,8] and secondary deuterium isotope effects.[9] To determine the amount of return requires an independent measure of (a) the total rate of ionization or (b) the rate of re-formation of substrate by ion-pair return.

With optically active substrates that give symmetrical (bridged[2b,8b] or allylic[7,10]) carbonium ions, the rate of loss of optical activity (eq 1) corresponds to the total rate of ionization providing that the ion pair, as well as the unperturbed cation, is symmetrical. With systems that do not isomerize, ion-pair return does not disturb the rate of solvolysis (eq 2) and the rate of return, which corresponds to rate of racemization (eq 3), is obtained indirectly as the difference between rates of ionization (k_α) and solvolysis (k_t), i.e., $k_{rac} = k_\alpha - k_t$.[10] Alternatively, the rate of racemization can be obtained directly by isolating samples of unsolvolyzed substrate throughout the reaction and determining k_{rac} from the rotations.[8a]

Another direct method for measuring return is determining the rate of randomization of carboxyl or sulfonate oxygen atoms (k_{eq}) starting with discretely ^{18}O-labeled *p*-nitrobenzoate[8a,10] (eq 4) or arylsulfonate.[8b] Providing the oxygen atoms in the anion are equivalent in the ion-pair intermediate, k_{eq} corresponds to total return. The distinguishing feature of this method is that it is applicable to achiral as well as chiral nonrearranging systems.

$$(+)\text{-}RX \xrightarrow{k_\alpha} \text{inactive products} \quad (1)$$

$$R\text{–}X \xrightarrow{k_t} \text{solvolysis products} \quad (2)$$

$$(+)\text{-}RX \xrightarrow{k_{rac}} (\pm)\text{-}RX \quad (3)$$

$$R\text{—}^{18}OCOAr \xrightarrow{k_{eq}} R\text{—}^{18}OC^{18}OAr \quad (4)$$

Since the oxygen atoms in the intermediate are not always equivalent,[12] k_{eq} is a lower limit for return—excess rebonding of the original oxygen and carbon atoms is undetected. Similarly, k_α is a lower limit for ionization (or k_{rac}

for return) because even though the unperturbed bridged or allylic cation is symmetrical the ion pair may not be. Indeed, there is evidence that this is the case in some allylic systems.[13]

To obtain information regarding the fraction of return detected by oxygen equilibration we have compared k_{eq} with return measured by independent methods in allylic systems and systems involving symmetrical bridged cations.[8b] For *p*-nitrobenzoates the amount of equilibration associated with return ranges from nil for a case involving rearrangement to a strained carbonium ion[14] to partial for several allylic systems[10] and one rearranging system in which the anion migrates a considerable distance,[15] and evidently to complete in systems that give relatively stable (delocalized) carbonium ions.[5,10b,12]

We now report a comparison of k_{eq} with an independent measure of a lower limit of return for solvolysis of 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate (I-OPNB), a system which does not involve a symmetrical bridged ion but one in which ion-pair return results in racemization of the unsolvolyzed ester.[11]
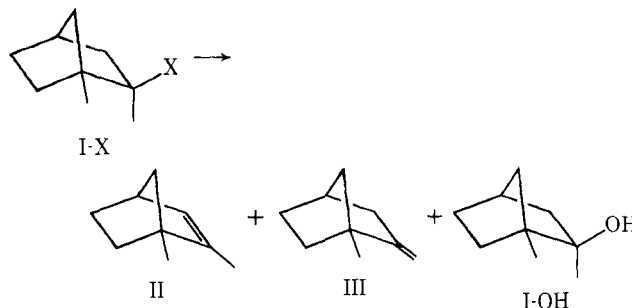
The pertinent rate constants for solvolysis of I-OPNB in 90% aqueous acetone at 78° are shown in Table I. The titrimetric rate constants (k_t) were steady up to 80% solvolysis, which shows that the structure of the substrate is preserved throughout the reaction. A control experiment with ether-^{18}O labeled I-OPNB showed that solvolysis involves exclusive alkyl–oxygen cleavage.

For the polarimetric experiments the solvent contained a 50% excess of 2,6-lutidine to neutralize the acid produced

Table I
Rate Constants for Solvolysis of
1,2-Dimethyl-*exo*-2-norbornyl *p*-Nitrobenzoate
in 90% (v/v) Aqueous Acetone at 78.45°

Rate constant	$10^6 \ k, \ \text{sec}^{-1}$ [a]
k_α	17.2 ± 0.1
k_t	12.4 ± 0.1
k_rac	5.2 ± 0.4
k_eq	2.6 ± 0.3
k_exc [b]	$6.0^{b,c}$

[a] Average (and average deviations) of two to six independent experiments. [b] Second-order rate constant, 10^6 l. M^{-1} sec^{-1}. [c] Average value for one kinetic experiment.

by solvolysis. Under these conditions the products are optically stable—final rotations and product distributions remained constant for periods of several solvolytic half-lives. Since product distributions, final rotations, and k_α are independent of the 2,6-lutidine concentration over the range 0.08–0.6 M, it appears that the lutidine has no important effect on the solvolysis. Under these conditions solvolysis gives 14% I-OH, 50% 1,2-dimethyl-2-norbornene (II), and 36% 1-methyl-2-methylenenorborene (III). As can be seen in Table I, $k_\alpha > k_t$, which means that ion-pair return results in racemization of the unsolvolyzed ester.

The rate of racemization (eq 3) was determined directly from rotations of isolated samples of unsolvolyzed ester. Control experiments showed that isolation of active samples did not alter the optical purity. It is noteworthy that k_rac obtained directly is in good agreement with $k_\alpha - k_t$. This is further evidence that 2,6-lutidine has no important effect on k_α.

The rate constant for equilibration of the carboxyl oxygen atoms (k_eq) was determined with carbonyl-^{18}O labeled I-OPNB. Because of the high k_t/k_eq ratio this reaction could only be followed to ~22% reaction (75% solvolysis). The value in Table I is the average of three independent determinations.

The second-order rate constant for exchange (k_exc) between I-OPNB and p-nitrobenzoic acid was determined by the method used earlier.[16] Only 0.14% exchange resulted when a solution of 0.007 M I-OPNB and 0.0035 M p-nitrobenzoic acid-^{14}C was heated for one solvolytic half-life. This shows that exchange between unsolvolyzed ester and acid produced by solvolysis is insignificant and establishes that reactions 3 and 4 are intramolecular.

As reported earlier,[11] optically active I-OPNB gives active products; the E1 product (III) is formed with ~63% and the SN1 product (I-OH) with ~9% retention of configuration. The other E1 product (II) is also active; however, the optical purity has not been determined. The formation of active products shows that ionization gives the asymmetric classical ion instead of a symmetrical bridged ion. The partial loss of optical configuration evidently results from interconversion of enantiomeric classical ions (Wagner–Meerwein rearrangement) in competition with the product-forming steps. The different optical purities of the E1 and SN1 products shows that they are derived from different intermediates. The interpretation proposed earlier[11,17] is summarized in the accompanying scheme. This suggests that most, or all, of the E1 product is derived from the initially formed intimate ion pair and the SN1 product is formed from a solvent-separated ion pair or the dissociated carbonium ion. The additional dissociation required for substitution is accompanied by additional racemization. The absence of exchange suggests that there is no external ion-pair return and establishes that there is no external re-

turn. This is not surprising because the equilibrium constant for protonation of the basic anion ($1/K_A$) is very large and consequently the anion concentration remains low throughout the solvolysis.

$$R\text{-}X \rightleftharpoons [R^+X^-] \underset{?}{\rightleftharpoons} [R^+||X^-] \longrightarrow R^+ + X^-$$

E1 product   SN1 product
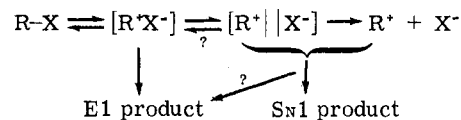
The rate of carboxyl oxygen equilibration (eq 4) is about half that of racemization (eq 3) and thus corresponds to the rate of interconversion of enantiomers. This is apparently a coincidence because we cannot imagine a plausible process (consistent with the principle of microscopic reversibility) that would give complete equilibration only when one enantiomer is converted to the other.[18]

In this system racemization detects more return than oxygen equilibration; however, k_rac does not correspond to total return. Clearly, substrate re-formed by ion-pair return must be at least as optically active as the E1 product (~63%). This is a lower limit because some E1 product may be formed from intermediates that are more racemic than the intimate ion pair. This means that k_rac corresponds to an upper limit of 37% of the total return. Thus, k_eq corresponds to an upper limit of 20% of the return. Or, to put it another way, at least 90% of the re-formed substrate has the original labeling pattern and 10% has inverse labeling. From this we conclude that in trialkylcarbinyl p-nitrobenzoates, oxygen equilibration correspond to only a fraction of the total return from product-forming intermediates.

Experimental Section

Oxygen-18 contents and distributions were determined as described earlier.[10,12] The solvent, 90% aqueous acetone (v/v), was prepared as described earlier.[16a]

Compounds. The samples of racemic I-OH, mp 104–106°, (−)-I-OH, mp 104–105°, [α]^{30}D −22.6° (c 7.3, CHCl$_3$), and (+)-I-OPNB, mp 143–144°, [α]^{30}D 37.3° (c 5.5, CHCl$_3$), used in this work were described earlier.[20] Less active samples of (+)-I-OPNB and samples of (−)-I-OPNB were also used. Racemic I-OPNB, mp 128–129.5° (lit. mp 132.5–133°),[21] was prepared by the method[20] used to prepare optically active I-OPNB.

I-OPNB-*carbonyl*-^{18}O, mp 127–128.5°, 3.704% excess ^{18}O, was prepared from I-OH and p-nitrobenzoyl-*carbonyl*-^{18}O chloride[19] in the usual manner[20] and obtained in 42% yield after purification by several recrystallizations from ether–pentane. A sample of this labeled ester was reconverted to I-OH by reduction with lithium aluminum hydride.[19] The resulting I-OH contained only 0.034% excess ^{18}O, which shows that >99% of the label was in the carbonyl position of the I-OPNB.

I-OPNB-*ether*-^{18}O was prepared as follows. A solution of 3.9 g of I-OH in a mixture of 102 ml of purified dioxane containing 25 ml of ^{18}O-enriched water (1.5% excess ^{18}O) and 4.96 g of 60% perchloric acid was warmed to 30° for 20 hr. Under these conditions (i.e., [HClO$_4$] = 0.23 M, [I-OH] = 0.22 M), the half-life for oxygen exchange is about 2 hr and exchange is about 10^3 times faster than exo → endo isomerization.[22] The solution was cooled, neutralized, diluted with 100 ml of water, and extracted with 200 ml of pentane. The pentane extracts were combined, shaken with 10% aqueous sodium carbonate, and dried. The resulting extract was concentrated to near dryness and the residue was purified by GC (20% KOH and 1% Carbowax 20M on firebrick). This preparation gave 2.3 g (59% recovery) of ^{18}O-labeled I-OH. Another preparation, using the same amounts but with more enriched ^{18}O water, gave 2.6 g (67%) of ^{18}O-labeled I-OH. Sublimation of the combined preparations gave 4.35 g (56%) of ^{18}O-labeled I-OH, mp 109–111°, 1.590% excess ^{18}O.

The above labeled I-OH was converted[20] to **I-OPNB-*ether*-^{18}O** in 60% yield, mp 130–131°, 1.691% excess ^{18}O.[23]

Kinetic Experiments. A. Titrimetric Rates. These reactions were followed as described earlier.[10,12] Rate constants (k_t) were independent of initial concentration over the range 0.026–0.07 M.

B. Polarimetric Rates. The polarimetric rate constants (k_α) were determined as described earlier.[5] In these experiments the I-

OPNB concentration varied from 0.06 to 0.12 M and in all cases 50% excess 2,6-lutidine was present. The change in rotation was at least 0.7° and individual readings were obtained with a precision of ±0.002°. Good first-order behavior was observed and rate constants determined from rotations for 589 and 436 nm were indistinguishable. Over the indicated concentration range 50% excess 2,6-lutidine has no effect on the observed rate of change of rotation.

That the presence of the lutidine does not affect the product distribution and that the initially formed products are stable under these conditions was established as follows. 2,6-Lutidine was added to four samples of a 0.067 M solution of (+)-I-OPNB, $[\alpha]^{25}$D +27.14° (c 5.6, CHCl₃), in 90% acetone so that the final lutidine concentrations were 0.08, 0.14, 0.28, and 0.56 M. After heating for 8 half-lives for solvolysis (12 hr), the observed rotations of the four solutions varied only 0.007° (from 0.113° to 0.120°). Capillary GC showed that the product distributions were the same for the four samples. It was also shown that a synthetic mixture of optically active II, III, and I-OH in 90% acetone containing 0.07 M p-nitrobenzoic acid and 0.14 M 2,6-lutidine does not undergo change in rotation or composition when heated for a period corresponding to 8 half-lives for solvolysis (k_t).

C. Rates of Racemization. The rate constant for racemization of the unsolvolyzed I-OPNB (k_{rac}) during solvolysis can be determined from the constants for solvolysis (k_t) and mutarotation (k_α), i.e., $k_{rac} = k_\alpha - k_t$.[10] In the present work the rate of racemization was determined directly from rotations of isolated samples of unsolvolyzed ester.[8a] In this case, unlike for the polarimetric rates, 2,6-lutidine was not present. In a typical experiment 7-ml portions of 0.046 M (−)-I-OPNB, $[\alpha]^{25}$D −11.35° (c 10, CHCl₃), in 90% acetone were sealed in ampoules that had been previously flushed with nitrogen. The ampoules were placed in a thermostat and quenched at appropriate times by chilling in ice water. Each ampoule was treated as follows. The contents were transferred to a 50-ml flask and neutralized with 0.03 M sodium hydroxide and the flask was attached to a vacuum line (10^{-5} mm) for 24 hr. The solid residue was extracted with 10 ml of dry ether and the filtered extract was concentrated to dryness under reduced pressure (10^{-2} mm) to remove all traces of I-OH, II, and III. The residue, pure I-OPNB, was transferred to a 1-ml volumetric flask, weighed, and diluted to exactly 1 ml with chloroform. The chloroform solution was transferred to a 1-dm microcell and rotations were determined at 40° and 436 nm. The rate constant (k_{rac}) was calculated in the usual way from the rotations of the samples. The value of k_{rac} in the table is the average of four independent experiments in which initial I-OPNB concentrations varied from 0.046 to 0.072 M. The initial rotation was at least 1° and the reaction was followed to about 25% racemization, which corresponds to >50% solvolysis.

That the isolation procedure does not alter the optical purity of the unsolvolyzed ester was established as follows. Racemic I-OPNB was completely solvolyzed (16 half-lives) in 90% acetone. A solution of (−)-I-OPNB in 90% acetone was prepared and mixed with the above solvolysis mixture to give solutions with (−)-I-OPNB concentrations corresponding to 0, 25, 50, and 75% solvolysis. The (−)-I-OPNB was isolated from the racemic solvolysis products as described above and the specific rotations of the four samples of recovered (−)-I-OPNB were $[\alpha]^{25}_{436}$ −25.97, −26.15, −25.99, and −26.12°. This shows that the isolation and separation gives recovered I-OPNB without alteration of optical activity.

D. Rates of Carboxyl-Oxygen Equilibration. The equilibration rate constant (k_{eq}) was determined as described earlier.[10,12,16a] The samples of unsolvolyzed ester were isolated as described above. The residual recovered I-OPNB (∼1 g) was converted to about 150 mg of I-OH, which was purified by two sublimations, and the ¹⁸O content of the resulting I-OH[23] was determined in the usual manner.[12,19] The rate constant for equilibration (k_{eq}) was calculated as described earlier.[10,12,16a]

That isolation of the unsolvolyzed ¹⁸O-labeled I-OPNB does not alter the ¹⁸O content was established as follows. Unlabeled I-OPNB was solvolyzed completely (10 half-lives) and to this solution was added a solution containing an equal amount of I-OPNB-carbonyl-¹⁸O, 3.704% excess ¹⁸O. This corresponds to 50% solvolysis. The I-OPNB isolated as described above contained 3.684% excess ¹⁸O.

The ¹⁸O content of the unsolvolyzed labeled I-OPNB after 75% solvolysis was 3.638%. This shows that there is no loss of label, or enrichment due to an isotope effect,[10b] during solvolysis.

E. Rates of Exchange. A 25-ml solution of 0.0069 M I-OPNB and 0.0035 M of ¹⁴C-labeled p-nitrobenzoic acid in 90% acetone was placed in a 78.45° thermostat for 16 hr, which corresponds to

50% solvolysis. The unreacted I-OPNB was isolated as described above. The specific activities (dpm/mmol) for the ¹⁴C-labeled acid, recovered I-OPNB, and original I-OPNB were 111,500, 584, and 448. From these data the rate constant for exchange (k_{exc}) and percentage exchange at any stage of the reaction can be determined as described earlier.[16a]

Control Experiments Demonstrating Alkyl–Oxygen Cleavage. Solvolysis of optically active I-OPNB in 90% acetone gives I-OH with 9% retention of optical configuration.[11] That the excess retention in the SN1 product does not result from acyl oxygen cleavage was established by the following experiments.

A 0.07 M solution of the above I-OPNB-ether-¹⁸O and 0.1 M 2,6-lutidine in 90% acetone was placed in a 100° thermostat for 10 solvolytic half-lives. The resulting I-OH was isolated by extraction with pentane, concentration of the dried (MgSO₄) pentane extract, and separation from other volatile products by preparative GC (10-ft column packed with 20% KOH and 1% Carbowax M-40 on firebrick 30/60 at 80°). The isolated alcohol was sublimed four times, the last time from powdered potassium hydroxide. Capillary GC showed the product to be 99% pure. The observed ¹⁸O content was 0.014% excess ¹⁸O. The ¹⁸O content would be 0.11% excess ¹⁸O if the excess retention of optical configuration resulted from acyl-oxygen cleavage.

In another experiment 2.4 g of unlabeled I-OPNB was solvolyzed under the above conditions in the presence of 11.4 mg of ¹⁸O-labeled I-OH, 1.59% excess ¹⁸O. The added labeled I-OH corresponds to 9.2 ± 0.7% of the total I-OH after complete solvolysis and the expected ¹⁸O content of the isolated alcohol is 0.15 ± 0.01 providing that there is no loss of ¹⁸O during solvolysis or the subsequent isolation and purification. The observed ¹⁸O content of the I-OH isolated and purified as above (44 mg) was 0.132% excess ¹⁸O. This shows that the loss of ¹⁸O from the initially formed I-OH during solvolysis, isolation, and purification is negligible.

References and Notes

(1) This work was supported by the National Institutes of Health (GM 14134), the National Science Foundation (GP-21116X), and the Research Council of Croatia.
(2) (a) S. Winstein et al., *J. Am. Chem. Soc.*, **80**, 459 (1958), and earlier papers; (b) S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc., Spec. Publ.*, **No. 19**, 109 (1965).
(3) R. A. Sneen, *Acc. Chem. Res.*, **6**, 46 (1973).
(4) A. F. Diaz and S. Winstein, *J. Am. Chem. Soc.*, **91**, 4300 (1969); I. L. Reich, A. F. Diaz, and S. Winstein, *ibid.*, **94**, 2256 (1972).
(5) H. L. Goering, G. S. Koermer, and E. C. Linsay, *J. Am. Chem. Soc.*, **93**, 1230 (1971).
(6) A. Fava, "The Chemistry of Sulfur Compounds", Vol. II, N. Kharasch and C. Meyers, Ed., Pergamon Press, Oxford, 1966, p 73; L. A. Spurlock and T. E. Peaks, *Mech. React. Sulfur Compd.*, **3**, 161 (1968); S. G. Smith and J. P. Petrovich, *J. Org. Chem.*, **30**, 2882 (1965).
(7) H. L. Goering, *Rec. Chem. Prog.*, **21**, 109 (1960).
(8) (a) H. L. Goering and H. Hopf, *J. Am. Chem. Soc.*, **93**, 1224 (1971); (b) H. L. Goering and R. W. Thies, *ibid.*, **9**, 2968, 2967 (1968).
(9) K. Humski, V. Sendijarević, and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **95**, 7722 (1973).
(10) (a) H. L. Goering, M. M. Pombo, and K. D. McMichael, *J. Am. Chem. Soc.*, **85**, 965 (1963); (b) H. L. Goering, J. T. Doi, and K. D. McMichael, *ibid.*, **86**, 1951 (1964).
(11) H. L. Goering and K. Humski, *J. Am. Chem. Soc.*, **90**, 6213 (1968).
(12) H. L. Goering and E. C. Linsay, *J. Am. Chem. Soc.*, **91**, 7435 (1969).
(13) H. L. Goering and J. T. Doi, *J. Am. Chem. Soc.*, **82**, 5850 (1960); R. P. Anderson, Ph.D. Thesis, University of Wisconsin, Madison, Wisconsin, 1966.
(14) W. G. Dauben and J. L. Chitwood, *J. Org. Chem.*, **34**, 726 (1969).
(15) H. L. Goering and R. F. Myers, *J. Am. Chem. Soc.*, **91**, 3386 (1969).
(16) (a) H. L. Goering and J. F. Levy, *J. Am. Chem. Soc.*, **84**, 3853 (1962); **86**, 120 (1964); (b) H. L. Goering and M. J. Degani, *ibid.*, **91**, 4506 (1969).
(17) H. L. Goering and J. V. Clevenger, *J. Am. Chem. Soc.*, **94**, 1010 (1972).
(18) Formation of the enantiomer with inverse labeling, i.e., (d)-ROC¹⁸OAr ⇌ (l)-R¹⁸OCOAr, would result in $k_{rac} = k_{exc}$.
(19) H. L. Goering and M. M. Pombo, *J. Am. Chem. Soc.*, **82**, 2515 (1960).
(20) H. L. Goering, C. Brown, S. Chang, J. V. Clevenger, and K. Humski, *J. Org. Chem.*, **34**, 624 (1969).
(21) H. Toivonen, *Suom. Kemistil. B*, **33**, 66 (1960).
(22) H. L. Goering, C. Brown, and C. Schewene, *J. Am. Chem. Soc.*, **90**, 6214 (1968).
(23) It should be noted that the apparent ¹⁸O content of I-OPNB is 5.7% larger than that of the I-OH from which it was derived. As noted earlier (footnote 13, ref 10), different derivatives with the same ¹⁸O content often give different apparent ¹⁸O contents. However, for each derivative the apparent ¹⁸O contents are reproducible. For this reason, to determine accurate relative ¹⁸O contents (such as required for kinetic experiments), the same derivative should be used for all determinations.