Rearrangement Studies with Carbon-14. XXXIV.
The π Route to the Norbornyl Cation from Solvolyses of 2-(Δ^3-Cyclopentenyl)-2-^{14}C-ethyl p-Nitrobenzenesulfonate[1a]

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Received April 14, 1969*

Abstract: Solvolyses of 2-(Δ^3-cyclopentenyl)-2-^{14}C-ethyl p-nitrobenzenesulfonate (I-ONs-2-^{14}C) in 20% H$_2$O–80% acetone–NaHCO$_3$ and in HOAc–urea were investigated. Analyses of the isotopic distributions in the 2-exo-norbornyl products indicated the absence of any 3,2-hydride shift, the ^{14}C label being scrambled only over the C-3, C-5, and C-7 positions. More activity was observed at C-3 than C-7 and this can be accounted for by assuming product formation from edge-protonated nortricyclene and from the norbornonium ion (corner-protonated nortricyclene). Quantitative analysis of the data led to the conclusion that under the conditions employed, corner-protonated nortricyclene is more stable than edge-protonated nortricyclene, the equilibrium constants between these two protonated nortricyclenes being estimated to be 116 and 4.6 in favor of corner protonation for the two solvent systems employed. Qualitative mechanistic implications of the present results are also discussed in conjunction with earlier results obtained from solvolysis of I-ONs-2-^{14}C in unbuffered acetic or formic acid.

In 1961, Lawton[2a] and Bartlett and Bank[2b] independently reported the π-route formation of 2-exo-norbornyl products from the solvolyses of 2-(Δ^3-cyclopentenyl)ethyl p-nitrobenzenesulfonate (I-ONs) or p-toluenesulfonate (I-OTs). Subsequent studies by Bartlett and coworkers[3] on the kinetic behaviors of I-ONs, I-OTs, and related systems have provided strong evidence in favor of the symmetrical norbornonium ion as an intermediate in these reactions. The magnitude of the α-deuterium kinetic isotope effects observed in solvolyses of I-ONs has also been interpreted as favoring nonclassical ions.[4] The isotopic scrambling resulting from the acetolysis or formolysis of 2-(Δ^3-cyclopentenyl)-2-^{14}C-ethyl p-nitrobenzenesulfonate (I-ONs-2-^{14}C) was reported by Lee and Lam[5] in 1966. In this earlier work, the labeled substrate was solvolyzed under conditions similar to those used in previous kinetic studies[4] without the presence of any added salt such as NaOAc to neutralize the sulfonic acid liberated. Consequently, there is the possibility that subsequent ionization of the initially formed product could have occurred thus complicating the over-all isotopic distributions. The present paper reports the results from solvolytic studies on I-ONs-2-^{14}C under conditions which are more likely to be kinetically controlled.

Results and Discussion

The solvolysis of I-ONs-2-^{14}C was effected in 80% acetone–20% water (by volume) in the presence of NaHCO$_3$ at reflux temperature for 48 hr or in glacial acetic acid in the presence of urea[6] at 60° for 30 hr. The cyclized product, 2-exo-norbornyl alcohol or ace-

tate (II-OH-^{14}C or II-OAc-^{14}C), and some uncyclized and presumably isotopically unrearranged I-OH-2-^{14}C or I-OAc-2-^{14}C were obtained, the cyclized to uncyclized product ratios being about 3.5:1 and about 11:1, respectively, for the reactions carried out in H$_2$O–acetone–NaHCO$_3$ and in HOAc–urea. The norbornyl products were degraded as described previously[5,7] by conversion to cis-cyclopentane-1,3-dicarboxylic acid to cis-cyclopentane-1,3-diamine to succinic acid to ethylenediamine. In addition, the 2-norbornanone derived from the II-OH-^{14}C or II-OAc-^{14}C product was converted, by treatment with phenylmagnesium bromide, to 2-phenyl-2-endo-nobornanol[8] which was, in turn, oxidized to benzoic acid to give a direct measure of the ^{14}C activity at C-2. In this way, the ^{14}C activities present at C-2, C-3, C-1,4, C-7, and C-5,6 can be ascertained. The results are summarized in Table I.

Since no activity was located at the C-1, C-2, and C-4 positions of the norbornyl products obtained, the absence of 3,2-hydride shifts under the solvolytic conditions employed in the present work was unequivocally demonstrated. The ^{14}C labels in the resulting norbornyl skeleton were thus located only at the C-3, C-7, and C-5 positions. As pointed out in the previous work,[5] solvent capture by the initially formed norbornonium ion from I-ONs-2-^{14}C would give rise to II-OH or II-OAc with the label located at C-5. Subsequent equilibrations via Wagner–Meerwein and/or 6,2-hydride shifts would lead to the distribution of the label at C-3, C-5, and C-7. While the II-OH-^{14}C from solvolyses in H$_2$O–acetone–NaHCO$_3$ showed approximately equal amounts of label at C-3 and C-7 as expected from nonclassical norbornonium ions, the results observed in the II-OAc-^{14}C from solvolyses in HOAc–urea indicated a *greater* amount of label at C-3 than C-7 (Table I). Even a more marked difference in the amounts of activity located at C-3 and C-7 was

(1) (a) Supported by a grant from the National Research Council of Canada. (b) Holder of a Senior Research Fellowship of the National Research Council of Canada, 1969.
(2) (a) R. G. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961); (b) P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961).
(3) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *ibid.*, **87**, 1288 (1965); P. D. Bartlett and G. D. Sargent, *ibid.*, **87**, 1297 (1965).
(4) C. C. Lee and E. W. C. Wong, *ibid.*, **86**, 2752 (1964); *Tetrahedron*, **21**, 539 (1965).
(5) C. C. Lee and L. K. M. Lam, *J. Am. Chem. Soc.*, **88**, 2834 (1966).
(6) W. S. Trahanovsky, M. P. Doyle, and P. D. Bartlett, *J. Org. Chem.*, **32**, 150 (1967).

(7) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **76**, 4501 (1954).
(8) D. C. Kleinfelter and P. von R. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961).

Table I. [14]C Distributions[a] (Per Cent) in 2-exo-Norbornyl Products from Solvolyses of I-ONs-2-[14]C

| | C-2[b] | | C-3 | | C-1,4[c] | | C-7 | | C-5,6 | |
Reaction medium	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
H_2O–acetone–$NaHCO_3$	0.0	0.0	18.0	18.5	0.0	0.0	17.8	17.5	64.2	64.0
HOAc–urea	0.0	0.0	27.8	27.9	0.0	0.0	24.1	22.8	48.1	49.3

[a] The ^{14}C activities were assayed by a liquid scintillation counter. For the solvolyses in aqueous acetone, 100% corresponded to specific activities of 87,500 and 112,500 cpm/mmole in runs 1 and 2, while for the reactions in HOAc–urea, 100% corresponded to specific activities of 87,800 and 98,400 cpm/mmole in runs 1 and 2. [b] Essentially inactive (0 ± 0.1%) benzoic acid was obtained from the oxidation of active 2-phenyl-2-endo-norbornanol. [c] The activities of the succinic acid and ethylenediamine (assayed as the dibenzenesulfonamide) derived from each degradation differed by no more than 0 ± 0.2%, indicating essentially no ^{14}C activity at the C-1,4 positions of the norbornyl product.

found by Lee and Lam[5] in the unbuffered acetolysis and formolysis of I-ONs-2-[14]C.[9]

In considering the data of Lee and Lam,[5] Collins and Lietzke,[10] pointing out that the greater amount of label at C-3 than C-7 cannot be explained by a mechanism utilizing only nonclassical norbornonium ions, have suggested an alternative scheme involving 6,2 and Wagner–Meerwein shifts of classical norbornyl cations. Collins and Lietzke, however, stressed that they were taking no particular stand in favor of such a classical ion mechanism except by merely indicating that the classical ion scheme they proposed would be consistent with the tracer results of Lee and Lam, while a mechanism involving only nonclassical norbornonium ions would not. In view of the ready occurrence of 1,2-hydride shifts in a classical secondary–secondary cationic system[11] as well as the feasibility of exo–exo 3,2 shifts in the norbornyl system,[12] if classical norbornyl cations were to play a significant role in accounting for the isotopic scramblings, one might expect that at least some of the label would have been rearranged from C-3 to C-2 via 3,2-hydride shifts. Since the present results (Table I) have unequivocally eliminated any such 3,2 shifts, at least for the solvolysis of I-ONs-2-^{14}C in H_2O–acetone–$NaHCO_3$ or in HOAc–urea, classical norbornyl cations are not likely to be important intermediates.

The results obtained in the present work can be readily explained by invoking product formation from nonclassical norbornonium ions (corner-protonated nortricyclenes) as well as from edge-protonated nortricyclenes. The recent Raman spectral studies of Olah and coworkers[13] and the quantum mechanical calculations of Klopman[14] have led to the conclusion that both corner- and edge-protonated nortricyclenes may be stable intermediate species in the norbornyl cationic system. Six stereochemically different corner- and edge-protonated nortricyclene intermediates derived from I-ONs-2-^{14}C can be written as shown in Scheme I. Since IVa and IVc, as well as IIIb and IIIc, are isotopically indistinguishable, following the treatment used by Collins and Lietzke,[10] the mechanism may be rewritten

(9) The reproducibilities of the observed isotopic distributions from duplicate runs in the present and earlier[5] work are generally good; the maximum deviations from the mean per cent activities at the various positions are within ±1%. It is, therefore, reasonable to regard as significant differences of more than 2% in the observed per cent ^{14}C distributions. The difference between the per cent activities at the C-3 and C-7 positions of about 4–5% found in the present work in HOAc–urea, and the still higher differences in ^{14}C contents noted for these two positions in the previous work,[5] should be regarded as real differences.

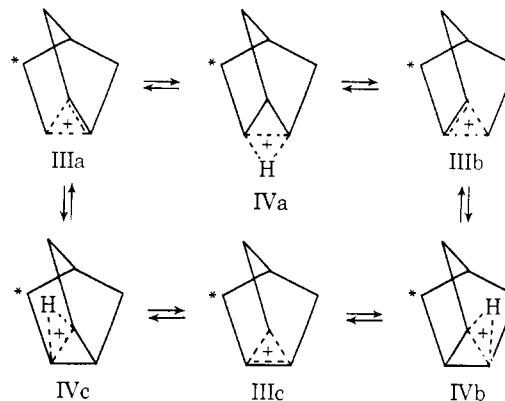(10) C. J. Collins and M. H. Lietzke, J. Am. Chem. Soc., **89**, 6565 (1967).
(11) G. J. Karabatsos, R. A. Mount, D. O. Rickter, and S. Meyerson, ibid., **88**, 5651 (1966).
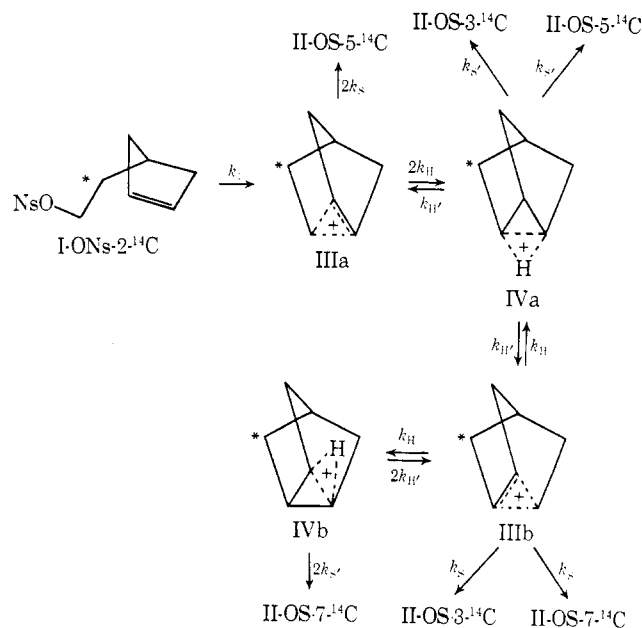(12) P. von R. Schleyer, ibid., **89**, 699 (1967).
(13) G. A. Olah, A. Commeyras, and C. Liu, ibid., **90**, 3882 (1968).
(14) G. K. Klopman, ibid., **91**, 89 (1969).

Scheme I

Scheme II

as shown in Scheme II. Again using the method of Collins and Lietzke,[10] for the mechanism depicted in Scheme II, if one lets m_3, m_5, and m_7 be the mole fractions of the norbornyl product with the ^{14}C label at C-3, C-5, and C-7, respectively, and if one also assumes that $k_S = k_{S'}$, it can then be shown (see Appendix) that $k_{H'}/k_S = 2m_7/(m_3 - m_7)$ and $k_H/k_S = 2(m_3 + m_7)/(m_5 - m_3)$.

From Table I, the mean values for the amounts of ^{14}C label located at C-3, C-7, and C-5 are calculated to be 18.3, 17.6, and 64.1%, respectively, for solvolysis in H_2O–acetone–$NaHCO_3$, and 27.8, 23.5, and 48.7%, respectively, for solvolysis in HOAc–urea. Using these averaged values, the calculated rate ratios, $k_{H'}/k_S$,

Table II. Rate Ratios for Solvolyses of I-ONs-2¹⁴-C According to the Mechanism Depicted in Scheme II

	H₂O–acetone–NaHCO₃	HOAc–urea
$k_{H'}/k_S$	186	22.6
k_H/k_S	1.6	4.9
$k_{H'}/k_H$	116	4.6

Table III. Calculated ¹⁴C Distributions for Solvolyses of I-ONs-2-¹⁴C in H₂O–Acetone–NaHCO₃ and in HOAc–Urea

Product from	—% contribution— H₂O–acetone	HOAc–urea	Calculated ¹⁴C, % — H₂O–acetone–NaHCO₃ — C-3	C-7	C-5	HOAc–urea C-3	C-7	C-5
IIIa	45.8	20.9			45.8			20.9
IVa	1.4	8.6	0.7		0.7	4.3		4.3
IIIa ⇌ IVa ⇌ IIIb ⇌ IVb	52.8	70.5	17.6	17.6	17.6	23.5	23.5	23.5
Calculated ¹⁴C distribution			18.3	17.6	64.1	27.8	23.5	48.7
Observed mean			18.3	17.6	64.1	27.8	23.5	48.7

second intermediates, IIIa and IVa, would have ¹⁴C label located, respectively, at C-5, and at C-3 and C-5. Further equilibration of IIIa ⇌ IVa ⇌ IIIb ⇌ IVb, which would imply the inclusion of Wagner–Meerwein as well as 6,2-hydride shifts, would give rise to a norbornyl product with equal amounts of label at C-3, C-5, and C-7. In Table III are shown the calculated contributions of the various intermediates in order to

k_H/k_S, and $k_{H'}/k_H$, are summarized in Table II. These treatments indicate that $k_{H'}$ is greater than k_H, suggesting that under the solvolytic conditions employed, the norbornonium ion or corner-protonated nortricyclene is more stable than the edge-protonated species. It is of interest to note that in a very recent 220-MHz nmr study on the addition of DCl to norbornene and nortricyclene, Brown and McIvor[15] obtained results which could be interpreted as indicating an irreversible leakage of edge-protonated nortricyclene to corner-protonated nortricyclene, suggesting that the latter species is more stable as is found in the present work. The ratio of $k_{H'}/k_H$ in Table II actually represents the equilibrium constant between corner- and edge-protonated nortricyclenes, and hence the corner-protonated species is favored at equilibrium over the edge-protonated species by factors of 116 and 4.6 in the two solvent systems employed. These results constitute the first quantitative values estimated for the equilibrium constant between corner- and edge-protonated nortricyclenes under solvolytic conditions.

It may also be of some interest to point out that in simple protonated cyclopropanes, edge protonation presumably accounts better for the observed products than corner protonation.[16] Probably, in the corner-protonated nortricyclene, the three-center bond among the three carbon atoms may be greatly improved by the forced proximity in a bicyclic system, whereas, in a simple cyclopropane, the three-center bond with one hydrogen and two carbon atoms may be of comparable or greater stability than a corner-protonated species. It is the competition between these two kinds of three-center bonds that determines the equilibrium represented by $k_{H'}/k_H$.

While the above treatment is capable of giving quantitative estimates of the various rate ratios pertinent to the mechanism outlined in Scheme II, it may also be of interest to interpret the results in a qualitative manner as was done previously by Roberts and coworkers[7] and by Lee and Lam.[5] Considering Scheme II, it is seen that the norbornyl product derived from the first and

give the isotopic distributions observed in the present work. It is worth noting from Table III that for the solvolysis in H₂O–acetone–NaHCO₃, the conditions most favorable for kinetic control, a larger proportion of the product could be regarded as being derived from the first intermediate IIIa.

Let us now consider the results reported by Lee and Lam[5] for the solvolysis of I-ONs-2-¹⁴C in unbuffered acetic or formic acid. In this earlier work, a direct determination of the ¹⁴C activity at C-2 was not carried out. The presence of small amounts of activity at C-1,4, however, suggested the occurrence of some 3,2-hydride shifts which together with the other possible rearrangement processes would render all seven carbon positions of the norbornyl skeleton isotopically equivalent. The amount of activity at C-1,4 in the norbornyl product from the formolysis of I-ONs-2-¹⁴C was sufficiently large and could be regarded as probably beyond any reasonable experimental errors, and this together with the 3,2-hydride shifts noted in the formolysis of 2-t-2-exo-norbornyl brosylate[17] would indicate that for the formolysis, some 3,2-hydride shifts have actually taken place. Possibly, such 3,2 shifts could have resulted from some involvement of the classical norbornyl cation formed during solvolysis in the highly ionizing formic acid as solvent. Calculations were carried out for the unbuffered acetolysis and formolysis of I-ONs-2-¹⁴C using the processes similar to those shown in Table III together with an additional process which rendered all seven carbon positions equivalent; the results obtained are given in Table IV.

There is an apparent anomaly in the treatment given in Table IV. For the acetolysis, no product was supposed to have been derived from the first intermediate IIIa, while for the formolysis, 7% of the product was apparently formed from this first intermediate. Such behaviors are not to be expected since HOAc is more nucleophilic than HCOOH. Because of such inconsistencies, although Lee and Lam[5] have considered edge-protonated nortricyclene as a possible explanation of the finding that more label was located at C-3 than C-7 in the norbornyl products from unbuffered acetolysis and formolysis of I-ONs-2-¹⁴C, an alternative explanation has been suggested. This alternative process was

(15) J. M. Brown and M. C. McIvor, *Chem. Commun.*, 238 (1969).

(16) (a) R. L. Baird and A. A. Aboderin, *J. Am. Chem. Soc.*, **86**, 252 (1964); (b) C. C. Lee and J. E. Kruger, *Tetrahedron*, **23**, 2539 (1967); (c) G. J. Karabatsos, J. L. Fry, and S. Meyerson, *Tetrahedron Lett.*, 3735 (1967).

(17) C. C. Lee and L. K. M. Lam, *ibid.*, **88**, 5355 (1966).

Table IV. Calculated [14]C Distributions for Unbuffered Acetolysis and Formolysis of I-ONs-2-[14]C Utilizing Edge-Protonated IVa as One of the Product-Forming Intermediates

Product from	% contribution In HOAc	In HCOOH	Calculated ^{14}C, % — Acetolysis C-2,3	C-1,4	C-7	C-5,6	Formolysis C-2,3	C-1,4	C-7	C-5,6
All C equivalent	3	12	0.9	0.9	0.4	0.9	3.4	3.4	1.7	3.4
IIIa	0	7								7.0
IVa	25	6	12.5			12.5	3.0			3.0
IIIa ⇌ IVa ⇌ IIIb ⇌ IVb	72	75	24.0		24.0	24.0	25.0		25.0	25.0
Calculated ^{14}C distribution			37.4	0.9	24.4	37.4	31.4	3.4	26.7	38.7
Observed mean[a]			37.8	0.9	24.8	36.5	31.4	3.4	26.5	37.7

[a] From ref 5.

termed a "concerted rearrangement" as depicted by V. It was visualized that the ion pair formed from I-ONs-2-^{14}C would have the negative counterion located quite

V
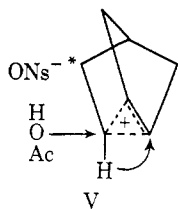
far from the developing positive charge and such a large charge separation might be alleviated by a process such as V. However, Collins and Lietzke[10] have pointed out that the small kinetic isotope effects reported for π-route acetolysis reactions[4,18] do not support a concerted hydrogen migration in the rate-determining step. While Lee and Lam[5] did not stress the point in their original discussions, the processes involving hydride shift and product formation as depicted by V implied the occurrence of these processes subsequent to the rate-determining ion-pair formation. The use of the term "concerted" by Lee and Lam was perhaps rather unfortunate. It was meant to denote 6,2-hydride shift together with product-forming solvent capture, with these processes taking place rapidly and almost simultaneously. An isotopically equivalent process would be a completed 6,2-hydride shift *followed* by product-forming reaction with solvent. Such a 6,2 shift followed by product formation does not differ so very greatly from the formation of product *via* edge-protonated nortricyclene which may be regarded as a "midway" 6,2-hydride shift followed by product formation. A "completed" 6,2-hydride shift, however, would amount to the formation of a classical norbornyl cation, and in the present mechanistic context, this could be regarded as a limiting case in the migration of hydrogen from C-6 to C-2. In the π route to the norbornyl cation from solvolysis of I-ONs-2-^{14}C, as indicated above, there is a large charge separation in the initially formed norbornonium nosylate ion pair and this charge separation may be decreased by the 6,2-hydride shift. Depending on the conditions of the reaction, product could arise at various stages of completion of the 6,2 shift along the reaction coordinate. For solvolyses under the more nucleophilic conditions as in H_2O-acetone-$NaHCO_3$ or in HOAc-urea, the norbornyl product obtained can be rationalized as being derived in part from the initially formed ion, from the symmetrical or

"midway" 6,2-shifted edge-protonated nortricyclene in which C-2 and C-6 are equivalent, and from completely equilibrating shifts that rendered C-3, C-7, and C-5 equivalent. On the other hand, when solvolysis of I-ONs-2-^{14}C was carried out in a more ionizing solvent where the lifetime of the ions could be longer, for a very short time, there may exist a species with unequal charge distribution at C-2 and C-6, the more the charge has shifted over to the side of the negative counterion, the greater will be the beneficial effect in reducing the charge separation in the initially formed ion pair from the π route. Thus for solvolysis in unbuffered HOAc or HCOOH instead of a contribution from the symmetrical edge-protonated nortricyclene, a process with more nucleophilic attack at the side nearer the counterion is possible, hence giving rise to more norbornyl product with the label at C-3 when the starting material is I-ONs-2-[14]C.

It may be worthwhile pointing out here that for the σ route, similar arguments as given above would suggest that 6,2 shifts will increase the charge separation, and the same force that favors the 6,2 shift in the π route will tend to suppress 6,2 shifts in the σ route, with the net result of more σ-route products being derived from Wagner–Meerwein type of intermediates. This prediction is in agreement with the isotopic scrambling results observed in the σ-route acetolysis of 2-*exo*-norbornyl brosylate labeled at the C-2 or C-2 and C-3 positions,[7,19] lesser amounts of the label being found at C-5,6 than at C-2,3 of the product.

For the purpose of qualitative discussion of the isotopic scrambling data from the solvolyses of I-ONs-2-^{14}C in unbuffered HOAc and HCOOH, a contributing process corresponding to the limiting case of a "completed" 6,2 shift may be included, although probably the ion responsible for this process is more likely to have an unequal charge distribution at C-2 and C-6 rather than a localized charge at one of these two positions. Thus modifying only the terminology used by Lee and Lam to designate the various contributing processes, the calculated ^{14}C distributions for the solvolyses of I-ONs-2-^{14}C in unbuffered HOAc and HCOOH are given in Table V.

From Tables III and V, it is seen that as the solvent is changed in the order of H_2O-acetone-$NaHCO_3$, HOAc-urea, HOAc, and HCOOH, the contributions to product formation from the initially formed ion IIIa are, respectively, 45.8, 20.9, 12, and 10%, while the contributions from the completely equilibrated process with C-3, C-7, and C-5 equivalent are, respectively, 52.8,

(18) K. Humski, S. Borcic, and D. Sunko, *Croat. Chem. Acta*, **37**, 3 (1965).

(19) C. C. Lee and L. K. M. Lam, *J. Am. Chem. Soc.*, **88**, 2831 (1966).

Table V. Calculated ^{14}C Distributions for Unbuffered Acetolysis and Formolysis of I-ONs-2-$^{14}C^a$

Product from	% contribution In HOAc	% contribution In HCOOH	Acetolysis C-2,3	Acetolysis C-1,4	Acetolysis C-7	Acetolysis C-5,6	Formolysis C-2,3	Formolysis C-1,4	Formolysis C-7	Formolysis C-5,6
All C equivalent	3	12	0.9	0.9	0.4	0.9	3.4	3.4	1.7	3.4
IIIa	12	10				12.0				10.0
Limiting 6,2 shift	13	3	13.0				3.0			
IIIa ⇌ IVa ⇌ IIIb ⇌ IVb	72	75	24.0		24.0	24.0	25.0		25.0	25.0
Calculated ^{14}C distribution			37.9	0.9	24.4	36.9	31.4	3.4	26.7	38.4
Observed mean			37.8	0.9	24.8	36.5	31.4	3.4	26.5	37.7

^{a} Same as Table II in ref 5, but with the designations given in column 1 modified.

70.5, 72, and 75%. These values are qualitatively as expected on the basis of the nucleophilic character and ionizing power of the various solvent systems employed. A final point relating to the nucleophilic character and ionizing power of these solvent systems may be made in terms of product composition. Earlier it was stated that the cyclized to uncyclized product ratios for solvolyses in H_2O–acetone–$NaHCO_3$ and in HOAc–urea were, respectively, about 3.5:1 and about 11:1. When the products from unbuffered solvolyses of I-ONs in HOAc and HCOOH carried out at 60° for 30 hr were analyzed, the ratios of cyclized norbornyl to uncyclized 2-(Δ^3-cyclopentenyl)ethyl products were about 26:1 and 1:0, respectively, no uncyclized product being detected in the formolysis reaction.

Experimental Section

Solvolysis in H_2O–Acetone–$NaHCO_3$. A solution of 4.46 g (0.015 mole) of I-ONs-2-^{14}C and 1.17 g (0.015 mole) of $NaHCO_3$ in 150 ml of 20% H_2O–80% acetone (by volume) was gently refluxed for 48 hr. H_2O (100 ml) was then added, and most of the acetone was distilled off. A further 50 ml of H_2O was introduced and the resulting material was saturated with NaCl before being extracted five times with 50-ml portions of ether. The combined extract was washed with H_2O and dried over anhydrous $MgSO_4$. After removal of the solvent, a small portion of the residual material was analyzed by vpc for 2-exo-norbornanol (II-OH-^{14}C) and 2-(Δ^3-cyclopentenyl)ethanol (I-OH-^{14}C) using an 8 ft $^1/_8$ in. diameter stainless steel column packed with 25% FFAP on acid-washed Chromosorb W, maintained at 150°. Under these conditions, the retention times of II-OH and I-OH were 16 and 21 min, respectively. To the main portion of the product after removal of the ether solvent, inactive II-OH (about 3 g) was added as carrier. The diluted cyclized product, II-OH-^{14}C (about 4 g), was then recovered by sublimation. After purification by resublimation, chromatographically pure II-OH-^{14}C was obtained. More inactive II-OH was added as carrier, if necessary, before this alcohol was utilized for the subsequent degradations.

Solvolysis in HOAc–Urea. A solution of 3.00 g (0.01 mole) of I-ONs-2-^{14}C and 1.20 g (0.02 mole) of urea in 30 ml of glacial acetic acid was heated at 60 ± 1° for 30 hr. The resulting solution was poured onto ice-water and then extracted five times with 50-ml portions of petroleum ether. The combined extract was washed successively with water, with 10% K_2CO_3 solution, and again with water before being dried over anhydrous $MgSO_4$. After removal of the petroleum ether, a small portion of the residual material was analyzed by vpc using the FFAP column as described above for 2-exo-norbornanol acetate (II-OAc-^{14}C) (retention time 19 min) and 2-(Δ^3-cyclopentenyl)ethyl acetate (I-OAc-^{14}C) (retention time 22 min). The main portion of the product was dissolved in anhydrous ether and reduced with lithium aluminum hydride to give II-OH-^{14}C which was isolated with the aid of inactive carrier.

Degradation of II-OH-^{14}C. A portion of each sample of II-OH-^{14}C derived from the various solvolyses was degraded to cis-cyclopentane-1,3-dicarboxylic acid (VI), to cis-cyclopentane-1,3-diamine (VII), to succinic acid (VIII), to ethylenediamine (IX) as described previously,[5,7] with the modification that the diamines VII and IX were assayed as their respective dibenzenesulfonamides instead of the dibenzamides. The dibenzenesulfonamide of VII melted at 142°. *Anal.* Calcd for $C_{17}H_{20}O_4N_2S_2$: C, 53.68; H, 5.26; N, 7.36; S, 16.84. Found: C, 53.80; H, 5.23; N, 7.18;

S, 16.55. The dibenzenesulfonamide of IX is a known derivative melting at 167–168°. The dibenzenesulfonamide derivatives have an advantage over the dibenzamides in that their purifications to constant specific activity required lesser numbers of repeated recrystallizations.

Another portion of each sample of II-OH-^{14}C was oxidized to norbornanone-^{14}C by CrO_3 in HOAc.[19] This ketone was, in turn, converted to 2-phenyl-2-endo-norbornanol and then oxidized to benzoic acid. Typical procedures are given below.

To a Grignard solution prepared from 3.8 g of bromobenzene and 0.8 g of Mg in 30 ml of anhydrous ether was added dropwise a solution of 2.0 g of norbornanone-^{14}C in 30 ml of anhydrous ether. The resulting mixture was stirred and refluxed overnight before being decomposed by an aqueous solution of NH_4Cl. The product was extracted with ether and the extract dried over anhydrous $MgSO_4$. After removal of the ether, the residue was distilled under reduced pressure. The 2-phenyl-2-endo-norbornanol, collected at 99–102° (28 mm), solidified on cooling and melted at 43–44° (lit.[8] mp 44.2–44.6°). The yield was 2.18 g (85%).

A mixture of 1.0 g of 2-phenyl-2-endo-norbornanol, 13 g of KOH, and 20 g of $KMnO_4$ in 40 ml of H_2O was heated under gentle reflux for 5 days.[20] The resulting material was cooled and then filtered. The filtrate was washed with ether to remove any unreacted alcohol and then acidified with H_2SO_4. The product was recovered by repeated extraction with ether. After drying over anhydrous $MgSO_4$, the ether was removed and the solid residue was purified by sublimation yielding 0.3 g (59%) of benzoic acid, mp 122°.

Appendix

With reference to Scheme II, assuming $k_S = k_{S'}$ and letting m_3, m_5, and m_7 be the mole fractions of II-OS-3-^{14}C, II-OS-5-^{14}C, and II-OS-7-^{14}C, respectively, the following equations can be written

$$d(\text{II-OS-3-}^{14}C)/dt = k_S(\text{IVa}) + k_S(\text{IIIb})$$

$$d(\text{II-OS-5-}^{14}C)/dt = 2k_S(\text{IIIa}) + k_S(\text{IVa})$$

$$d(\text{II-OS-7-}^{14}C)/dt = 2k_S(\text{IVb}) + k_S(\text{IIIb})$$

$$d(\text{IVa})/dt = 2k_H(\text{IIIa}) + k_H(\text{IIIb}) -$$
$$2k_{H'}(\text{IVa}) - 2k_S(\text{IVa})$$

$$d(\text{IIIb})/dt = k_{H'}(\text{IVa}) + 2k_{H'}(\text{IVb}) -$$
$$2k_H(\text{IIIb}) - 2k_S(\text{IIIb})$$

$$d(\text{IVb})/dt = k_H(\text{IIIb}) - 2k_{H'}(\text{IVb}) - 2k_S(\text{IVb})$$

Integrating between 0 and ∞

$$m_3 = k_S \int_0^\infty (\text{IVa})dt + k_S \int_0^\infty (\text{IIIb})dt$$

$$m_5 = 2k_S \int_0^\infty (\text{IIIa})dt + k_S \int_0^\infty (\text{IVa})dt$$

$$m_7 = 2k_S \int_0^\infty (\text{IVb})dt + k_S \int_0^\infty (\text{IIIb})dt$$

(20) The oxidation can be effected in a shorter time by $KMnO_4$ in dilute H_2SO_4. However, to eliminate any possibility of carbonium ion formation, acidic conditions were avoided.

$$2k_{\mathrm{H}}\int_0^\infty (\mathrm{IIIa})\mathrm{d}t + k_{\mathrm{H}}\int_0^\infty (\mathrm{IIIb})\mathrm{d}t -$$

$$2k_{\mathrm{H}'}\int_0^\infty (\mathrm{IVa})\mathrm{d}t - 2k_{\mathrm{S}}\int_0^\infty (\mathrm{IVa})\mathrm{d}t = 0$$

$$k_{\mathrm{H}'}\int_0^\infty (\mathrm{IVa})\mathrm{d}t + 2k_{\mathrm{H}'}\int_0^\infty (\mathrm{IVb})\mathrm{d}t -$$

$$2k_{\mathrm{H}}\int_0^\infty (\mathrm{IIIb})\mathrm{d}t - 2k_{\mathrm{S}}\int_0^\infty (\mathrm{IIIb})\mathrm{d}t = 0$$

$$k_{\mathrm{H}}\int_0^\infty (\mathrm{IIIb})\mathrm{d}t - 2k_{\mathrm{H}'}\int_0^\infty (\mathrm{IVb})\mathrm{d}t -$$

$$2k_{\mathrm{S}}\int_0^\infty (\mathrm{IVb})\mathrm{d}t = 0$$

Replacing the integrals by the symbols S_{IIIa}, S_{IVa},

S_{IIIb}, and S_{IVb} and solving the six simultaneous equations by elimination of these integrals will give

$$k_{\mathrm{H}'}/k_{\mathrm{S}} = 2m_7(m_3 - m_7)$$

and

$$k_{\mathrm{H}}/k_{\mathrm{S}} = 2(m_3 + m_7)/(m_5 - m_3)$$

Photoreactions of Nitroanisoles with Cyanide Ion. Studies of Products and Reaction Sequence[1]

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Abstract: Irradiation of an aqueous solution of 4-nitroanisole and potassium cyanide in the presence of air affords 2-cyano-4-nitroanisole. Under the same conditions 2-nitroanisole gives a mixture of 4-cyano-2-nitroanisole and 6-cyano-2-nitroanisole, and 3-nitroanisole gives 3-nitrobenzonitrile. The preferred point of attack is therefore *meta* to nitro in each instance. The course of the reaction of 4-nitroanisole was probed by investigating the effect of oxygen on the system, possible interactions of cyanide with ground-state 4-nitroanisole, and rates and quantum yields as a function of cyanide concentration. It was concluded that cyanide intercepts photoexcited 4-nitroanisole with high efficiency, forming an intermediate of short lifetime which is oxidized by molecular oxygen to 2-cyano-4-nitroanisole. Competition experiments utilizing cyanide with pyridine, 2,4,6-trimethylpyridine, and iodide provide evidence that pyridine and cyanide compete for the same excited species of 4-nitroanisole, that pyridine converts the excited species to ground-state 4-nitroanisole (as well as yielding substitution products), that the quenching reaction is subject to steric hindrance, and that iodide quenches excited 4-nitroanisole. Data from these experiments in conjunction with data from previous studies are used to construct a table of relative reactivities for several nucleophiles toward photoexcited 4-nitroanisole.

4-**N**itroanisole is inert toward common nucleophilic reagents in aqueous solution. On irradiation with ultraviolet light, however, it reacts readily with a variety of substances. With pyridine and 4-methylpyridine it affords N-(4-methoxyphenyl)pyridinium salts,[2] with hydroxide it yields 4-nitrophenoxide and 4-methoxyphenoxide,[2,3] and with alkylamines it gives the corresponding N-alkyl-4-nitroanilines,[4] as shown in Scheme I.

(1) This research was supported by a research grant from the National Science Foundation and by a Public Health Service Predoctoral Fellowship awarded to J. H. M. Part VII in series of Photoinduced Substitution. For Part VI see R. L. Letsinger and K. E. Steller, *Tetrahedron Lett.*, 1401 (1969).

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Scheme I
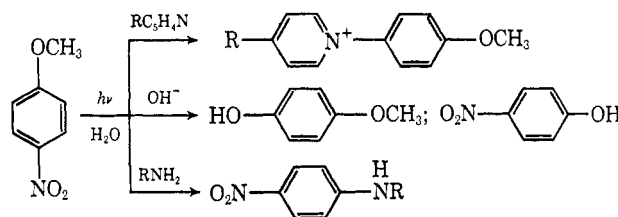
A survey of other nucleophiles revealed that cyanide ion is also highly reactive and that the course of the photochemical reaction of cyanide with 4-nitroanisole is quite different from that of the other nucleophiles. The present paper reports a detailed study of the cyanide reaction and describes competition experiments which bear on the general mechanism of reaction of nucleophiles with photoexcited 4-nitroanisole.[5]