gage in pπ–dπ bonding with a d orbital on each phosphorus.

The linear configuration, on the other hand, is indicative of sp hybridization on nitrogen. In this case, with both lone pairs now in unhybridized p orbitals, two perpendicular sets of P(dπ)–N(pπ)–P(dπ) interactions are possible. The distinct shortening of the P–N bond from the bent form to the linear form (1.575 (2)[22] vs. 1.539 (2) Å) could be due to enhanced pπ–dπ bonding effects in the linear compound, although some of the contraction may also be due to the difference in covalent radius between an sp^2 nitrogen and an sp nitrogen.

The fact that salts of both linear and bent forms can be derived from a common precursor, [(Ph$_3$P)$_2$N]$^+$Cl$^-$, indicates that linear–bent isomerization is taking place either in solution or during crystal formation. The ease in which this conversion takes place strongly suggests that the energy difference between the linear and bent forms is not large.[23]

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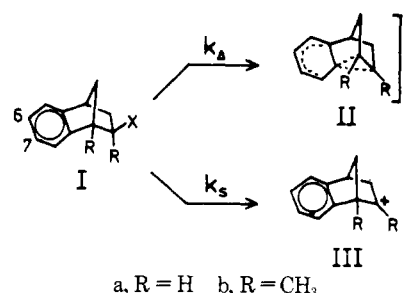
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Solvolysis of 1,2-Dimethyl-*exo*-2-benzonorbornenyl Derivatives. Direct Evidence for a Classical Carbonium Ion[1]

Sir:

There seems to be general agreement that solvolytic reactions of *exo*-2-benzonorbornenyl derivatives (Ia) involve assisted ionization $(k_\Delta)^2$ to give the symmetrical bridged nonclassical ion (IIa).[3] Pertinent evidence includes (a) effects of substituents in the aromatic ring on rates of solvolysis,[2b,c,d] (b) exo/endo rate ratios,[2] and (c) evidently the only capturable intermediate is symmetrical.[3]

a, R = H   b, R = CH$_3$

The situation is less clear for tertiary benzonorbornenyl systems. Electron releasing substituents at C-2 would be expected to increase k_s more than k_Δ and the point at which ionization changes from assisted $(k_\Delta > k_s)$ to unassisted $(k_s > k_\Delta)$ has been of interest for some time.[4] On the basis of substituent effects it has been concluded that assisted ionization is involved in the 2-methyl- and 2-phenyl-*exo*-2-benzonorbornenyl systems.[4a] In another investigation it was concluded that π participation is involved in the 6-methoxy-2-aryl-*exo*-2-benzonorbornenyl system[4b] but not if the 6-methoxy substituent is absent.[4c]
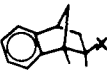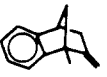
In earlier work[5] we showed that solvolysis of 1,2-dimethyl-*exo*-2-norbornyl derivatives involves the unsymmetrical classical ion and concluded that changing from the

Table I. Rate Constants for Solvolysis of Ib-Cl and Ib-OPNB[a]

Compound	Temp, °C	$10^4 k_t$, min^{-1}	$10^4 k_\alpha$, min^{-1}
		A. Methanol	
Ib-Cl	35.22	36.7 ± 1[b]	
Ib-Cl	45.20	115 ± 3[b]	389 ± 0.03[c,d]
Ib-Cl	53.48	304 ± 4	
Ib-OPNB	100.00	6.31 ± 0.01	9.95 ± 0.2[a,d,e]
Ib-OPNB	110.10	17.6 ± 0.3	29.6 ± 0.3[a,d,e]
		B. 90% Acetone (v/v)	
Ib-OPNB	100.00	0.762[f]	.903 ± 0.003[d-f]
Ib-OPNB	110.10	2.15[f]	2.73 ± 0.02[d-f]

[a] Substrate concentration 0.004 M. [b] Average of two independent experiments. [c] [Ib-Cl] = 0.07 M. [d] Solvent contained ~20% excess 2,6-lutidine. [e] Average of constants for rotations at four wavelengths. [f] [Ib-OPNB] = 0.02 M.

Table II. Rotations[a] and Optical Purities (OP) of Solvolysis Products Derived from Optically Active Ib-Cl and Ib-OPNB

(−)-Ib-X		(−)-IV	+	V	+	(−)-Ib-OS
$[\alpha]^{25}$D (% OP)[b]		$[\alpha]^{25}$D (% OP)				$[\alpha]^{25}$D (% OP)
A. Ib-Cl[c]	CH₃OH[d] (45°)	18% IV		+		82% Ib-OCH₃[e]
42.8° (16)[f]		33.4° (12)				0.35° (0.5)
42.8° (16)[f]		36.1° (13)				0.46° (0.7)
−31.8° (13)[f]		−24.7° (9)				−0.32° (0.5)
B. Ib-OPNB[g]	CH₃OH[d] (100°)	25% IV		+		75% Ib-OCH₃[e]
−86.4° (46)		−75° (26)				−2.78° (4)
C. Ib-OPNB[h]	90% acetone[d] (110°)	81% IV	+	13% V	+	6% Ib-OH[e]
−114.6° (76)		−128° (45°)				
−116.1° (77)		−139° (49)				

[a] Rotations are for CHCl₃ solutions. [b] Average optical purities for complete solvolysis determined by multiplying initial OP by k_t/k_α.[12] [c] [Ib-Cl] = 0.03 M. [d] Solvent contained ~20% excess 2,6-lutidine. [e] Product compositions determined by gc. [f] These optical purities are lower limits based on OP of IV derived by E2 elimination. [g] [Ib-OPNB] = 0.005 M. [h] [Ib-OPNB] = 0.02 M.

parent secondary to the tertiary system results in change from assisted to unassisted ionization.[6,7] Independent evidence bearing on this point has appeared in the meantime.[8]

We now wish to report that solvolysis of optically active 1,2-dimethyl-*exo*-2-benzonorbornenyl chloride (Ib-Cl) and *p*-nitrobenzoate (Ib-OPNB) gives optically active products. This is direct evidence that solvolysis involves the asymmetric classical ion (IIIb), rather than the symmetrical nonclassical ion (IIb). Thus, evidently ionization changes from assisted in the parent secondary system (Ia-X)[2] to unassisted in the tertiary system (Ib-X).

Optically active Ib-Cl was obtained by hydrochlorination (−78°)[5b] of optically active 1-methyl-2-methylenebenzonorbornene (IV).[9] The optical purity of Ib-Cl was determined by reconversion to IV with potassium *tert*-butoxide in dimethyl sulfoxide (45°). The (+)-IV → (+)-Ib-Cl → (+)-IV sequence resulted in about 20% loss of optical configuration. Presumably this loss occurs during hydrochlorination because dehydrochlorination appears to be an E2 elimination—no reaction occurs in the absence of base. Samples of active Ib-Cl, mp 48–50°, were shown to be homogeneous by solvolysis equivalent, elemental analysis, and spectral (nmr, ir, and mass spectral) properties.

The optically active tertiary *p*-nitrobenzoate (Ib-OPNB) was prepared[5a] from active Ib-OH[9] and purified by chromatography (silica gel) and recrystallization. The optical purity (as high as 98%) was determined directly with an optically active nmr shift reagent, Eu(facam)₃.[10,11] That the active Ib-OPNB, mp 180°, was homogeneous was clear from the spectral properties and solvolysis equivalent.

Titrimetric (k_t) and polarimetric (k_α) rate constants for methanolysis of Ib-Cl and Ib-OPNB and solvolysis of Ib-OPNB in 90% (v/v) aqueous acetone are presented in Table I. All rates are first order and in each case $k_\alpha > k_t$. Thus, ion-pair return results in racemization of the unsolved substrate.

The product studies are summarized in Table II. In these experiments the solvent contained a slight excess of 2,6-lutidine. Under these conditions the products are optically stable. Since increase in lutidine concentration up to 0.1 M has only a slight (retarding) effect on k_α, presumably it has no important effect on solvolysis. Product distributions and optical purities (per cent OP) of reactants and products are shown in the table. Optical purities of Ib-OH, Ib-OCH₃, and IV were determined directly from their rotations.[11] The values for Ib-Cl and Ib-OPNB are average optical purities for complete solvolysis obtained by multiplying initial values by k_t/k_α.[5,12]

Table II shows that in every case the E1 product (IV) is considerably more active (57–81% retention) than the SN1 product (3–9% retention). Comparison of results for Ib-Cl and Ib-OPNB shows that change in leaving group, which changes ionization rates >10⁴-fold (50°), has little effect on the activities of the products. The present results are remarkably similar to those reported earlier for the 1,2-dimethylnorbornyl system with regard to activities of E1 and SN1 products. As noted earlier,[5] it is clear that E1 and SN1 products are derived from different intermediates. Our earlier interpretation[5] appears adequate.

For reasons given earlier,[5b] it seems implausible that the partial loss of activity results from parallel assisted and unassisted processes. Rather the results indicate that ionization is totally unassisted and that partial loss of configuration results from racemization of intermediates in competition with solvent capture.

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