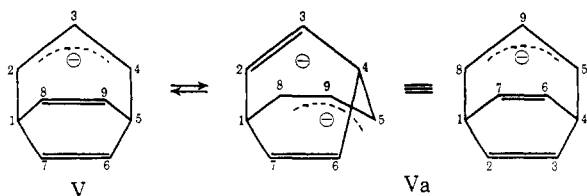


equivalently *via* a barbaralyl intermediate ($V \rightleftharpoons Va \rightleftharpoons$ etc.). This matter, together with the synthesis of metal complexes of IV, is presently under investigation.



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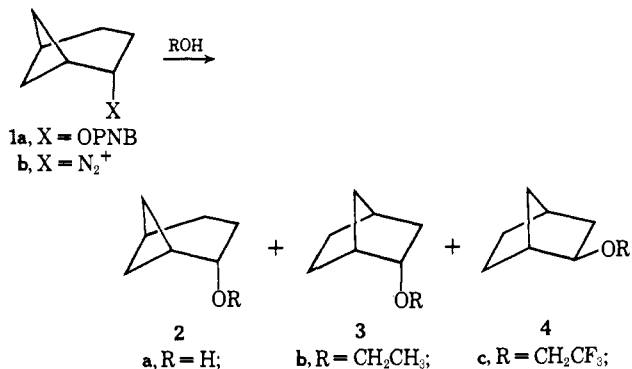
Received August 12, 1968

A Novel σ Route to the Norbornyl Cation

Sir:

We have investigated the formation of norbornyl cations by rearrangement of various norpinyl (bicyclo[3.1.1]heptyl) precursors.

Tosylate (TsCl, pyridine, 0°) of norpinan-2-ol (2a)¹ afforded *endo*-norbornan-2-yl tosylate, indistinguishable by melting point and ir from an authentic sample.^{2,3} The *p*-nitrobenzoate of norpinan-2-ol (1a), mp 89–90°, was solvolyzed in 66.7% aqueous acetone (sealed tube, 120°, 240 hr, *ca.* 30% conversion) to give 2a (3.5%), 3a (34%), and 4a (62.5%). Attempts to separate the recovered mixture of *p*-nitrobenzoates by tlc failed, but reduction with LiAlH₄ afforded 2a (58.2%), 3a (36.5%), and 4a (5.3%).



Rearrangement with internal return, producing *endo*-norbornan-2-yl *p*-nitrobenzoate, appears to be a major primary step in the solvolysis of 1a.⁴ Under the conditions specified above, *endo*-norbornan-2-yl *p*-nitrobenzoate solvolyzes to the extent of 1.4% to give 4a. Obviously most of the 4a produced in the solvolysis of 1a is *not* formed by way of an *endo*-2-norbornyl intermediate.

This conclusion is supported by the decomposition of 2-norpinyl diazonium ions (1b), where internal return of the leaving group should not occur. A convenient

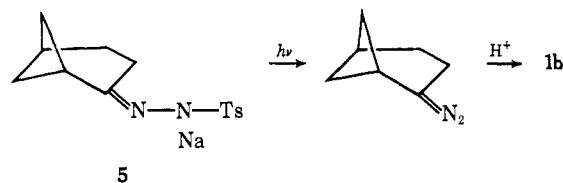
(1) H. Musso, K. Naumann, and K. Grychtol, *Chem. Ber.*, **100**, 3614 (1967), and unpublished results.

(2) S. Winstein and D. Trifan, *J. Amer. Chem. Soc.*, **74**, 1147 (1952).

(3) Related observations have been made in the brosylation of the nopinols by P. von R. Schleyer, W. E. Watts, and C. Cupas, *ibid.*, **86**, 2722 (1964); *cf.* also ref 4.

(4) Our results resemble those of E. C. Friedrich and S. Winstein, *ibid.*, **86**, 2720 (1964), in the nopinyl (6,6-dimethylbicyclo[3.1.1]heptyl) series.

method of generating 1b is the photolysis of norpinan-2-one¹ tosylhydrazone, mp 200–202°, in alkaline solution. Photolysis of tosylhydrazone salts is known to give diazoalkanes.⁵ Diazolokanes are sufficiently basic for protonation even in alkaline aqueous or alcoholic solutions.⁶ This deamination procedure ensures kinetic control and permits variation of the attacking nucleophile.



Photolyses of 5 have been carried out in water-dimethoxyethane, ethanol, and trifluoroethanol (Table I). In the H₂O–DME experiments, variation of the

Table I. Product Distribution (%) in the Photolysis^a of 5

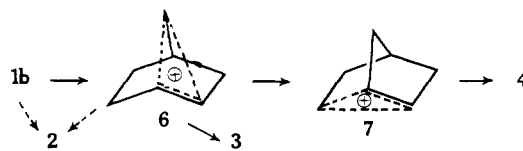
Solvent	Equiv of base	Hydrocarbons ^b	2	3	4
H ₂ O–DME (6:4)	1.9	4.7	2.6	40.0	52.7
	10.0	13.4	2.5	36.2	47.9
CH ₃ CH ₂ OH	2.5	42.6	11.4	24.3	20.7
CF ₃ CH ₂ OH	6.4	34.0	4.6	10.3	51.1

^a Water-cooled medium-pressure mercury arc (Hanau), quartz vessels, 20°. ^b Major components were nortricylcene, norpinene-2, and tricyclo[3.2.0.0^{2,7}]heptane, identified by comparison with authentic samples.

alkali concentration from 2 to 10 equiv had only a small effect on the product distribution. The *exo/endo* ratio of the norbornane derivatives depended markedly on the nucleophilicity of the solvent. Trifluoroethanol, a poor nucleophile,⁷ afforded predominantly *exo*-2-norbornyl trifluoroethyl ether (4c).

Photolysis of 5 in D₂O–DONa–DME led to the incorporation of 0.91 atm of D in 3a and 4a. Quantitative nmr analysis revealed that 3a-d did not contain deuterium in position 2 (α to OH). The simplified H-2 signal of 3a-d (approximately a doublet of doublets), as compared with 3a, indicates that most of the deuterium in 3a-d occupies the bridgehead position. In contrast, 4a-d contained 43 \pm 5% of its D in position 2.

Obviously, most of the 4a comes from the well-known bridged (or rapidly equilibrating) norbornyl cation 7, which reacts with high *exo* stereospecificity. In our reaction sequence, 7 appears to be preceded by a norbornyl cation of high *endo* stereospecificity which may be pictured as the bridged species 6.⁸ Clearly, our



(5) W. G. Dauben and F. G. Willey, *ibid.*, **84**, 1497 (1962).

(6) W. Kirmse and H. A. Rinkler, *Ann.*, **707**, 57 (1967).

(7) F. L. Scott, *Chem. Ind.* (London), 224 (1959); W. S. Trahanovsky and M. P. Doyle, *Tetrahedron Lett.*, 2155 (1968).

(8) Formation of the norpinane derivatives 2 may proceed *via* 6, but direct displacement on 1a,b is also a possible path.

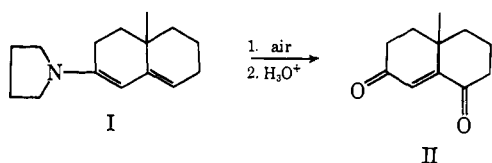
results are incompatible with only one (classical) norbornyl intermediate.

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Autoxidation of Enamines and Schiff Bases of α,β -Unsaturated Ketones. A New Synthesis of Unsaturated 1,4-Diones

Sir:

Enamines and enolate anions derived from α,β -unsaturated ketones undergo electrophilic attack at the α -carbon atom.¹ We wish to report that, unlike the autoxidation of enolate anions which leads mainly to the α -keto products,² the enamines undergo autoxidation giving mainly the γ -keto products, which on hydrolysis provide the corresponding 1,4-diones. Bubbling a slow stream of air through a 0.01 *M* benzene solution of the pyrrolidine enamine of 10-methyl- $\Delta^{1(9)}$ -octalone-2 (I) for 16 hr at room temperature and subsequent hydrolysis with dilute acetic acid gave 10-methyl- $\Delta^{1(9)}$ -octalin-2,8-dione (II) [mp 70–72°; ν_{\max} (film) 1680 cm^{-1} ; $\lambda_{\max}^{\text{MeOH}}$ 250 μm (ϵ 11,300); δ (CDCl_3 , Me_4Si reference) 6.3 (vinylic H, sharp, 1 H) and 1.26 (angular CH_3 , 3 H)]. The amount of the dione produced was rather low (20%) but addition of a catalytic amount of ferric chloride, cupric acetate, or cupric chloride caused a pronounced enhancement in the oxidation rate. Addition of a 0.1 molar equiv of these catalysts to the benzene solution of the enamine I to which a minimum amount of a cosolvent³ such as hexamethylphosphoramide or methanol was added to keep the solution homogeneous led to the dione in 80–85% yield⁴ after 1 hr. The reaction proceeds equally well



in the dark, thus excluding the possibility of any photosensitized oxidation.⁵ Since an ionic reaction between the molecular oxygen and the enamine violates the spin conservation rule and the electrophilic attack on the enamines of α,β -unsaturated ketones occurs at the α -carbon atom,¹ this reaction is most likely a free-radical chain process,⁶ and may proceed *via* the radical cation III as outlined in Scheme I.

(1) J. A. Marshall and W. S. Johnson, *J. Org. Chem.*, **28**, 421 (1963); G. Stork and G. Birnbaum, *Tetrahedron Lett.*, 313 (1961); S. K. Malhotra and H. J. Ringold, *J. Amer. Chem. Soc.*, **85**, 1538 (1963); **86**, 1997 (1964); H. J. Ringold and S. K. Malhotra, *ibid.*, **84**, 3402 (1962).

(2) B. Camerino, B. Patelli, and R. Sciaky, *Tetrahedron Lett.*, 554 (1961).

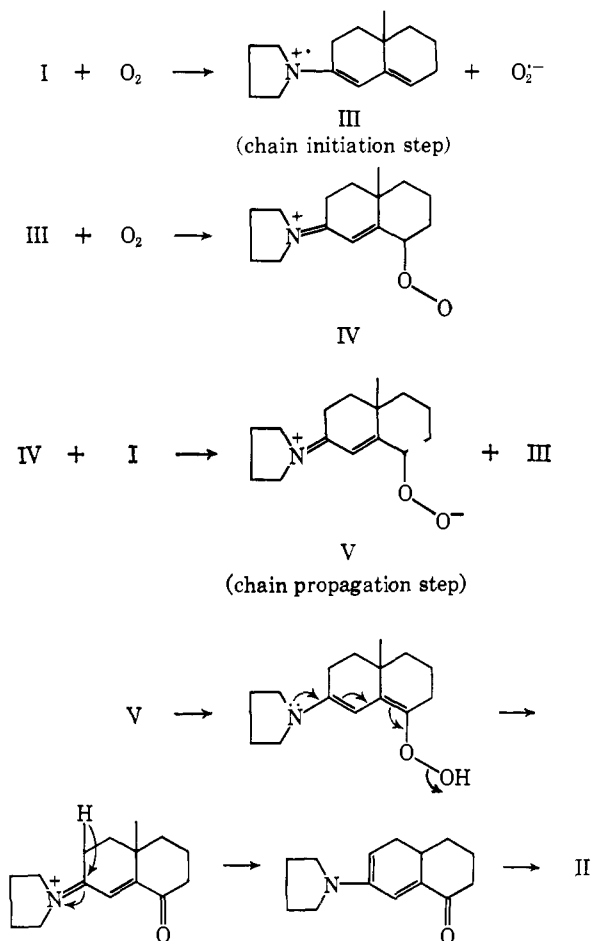
(3) Addition of cosolvents alone failed to show any noticeable increase in the yield of the product.

(4) The reported yields are the values obtained from several runs.

(5) For recent references on the photosensitized oxygenation of enamines, see C. S. Foote and J. W. P. Lin, *Tetrahedron Lett.*, 3267 (1968), and J. E. Huber, *ibid.*, 3271 (1968).

(6) For a review on the autoxidation of carbanions involving free-radical chain processes, see G. A. Russell, E. G. Janzen, A. G. Ames, E. J. Geels, A. J. Moye, S. Mak, and E. T. Strom, "Selective Oxidation Processes," *Advances in Chemistry Series*, No. 51, American Chemical Society, Washington, D. C., 1965, pp 112–171.

Scheme I



The striking catalytic effect of the metal ions such as Cu^{2+} and Fe^{3+} may be attributed to their ability to accept an electron from the enamine in the chain-initiation step.⁶ Similar autoxidation of the morpholine enamine of 10-methyl- $\Delta^{1(9)}$ -octalone-2 was slightly slower than that of III, the dione being formed in 65% yield after 1 hr.

In a similar manner, several Δ^4 -3-keto steroids have been oxidized *via* their corresponding enamines to 6-keto derivatives in 65–75% yield. For example, Δ^4 -cholesten-3-one was oxidized to Δ^4 -cholestene-3,6-dione⁷ and testosterone to 6-ketotestosterone.⁸ Progesterone and Δ^4 -androstene-3,17-dione were oxidized to Δ^4 -pregnene-3,6,20-trione⁹ and Δ^4 -androstene-3,6,17-trione,⁹ respectively.

We also wish to report that the autoxidation of the Schiff bases of α,β -unsaturated ketones also involves attack at the γ position, the product on hydrolysis in acidic medium giving the corresponding unsaturated 1,4-dione. For example, bubbling a slow stream of air through the 0.01 *M* benzene solutions of benzylamine Schiff bases of testosterone and Δ^4 -cholesten-3-one for 24 hr at room temperature followed by hydrolysis with dilute acetic acid led to 6-ketotestosterone⁸ and Δ^4 -cholestene-3,6-dione,⁷ respectively, in 70–75% yield. Benzylamine and cyclohexylamine Schiff bases of 10-

(7) L. F. Fieser, *Organic Syntheses*, Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1953, p 189.

(8) A. Butenandt and B. Riegel, *Ber.*, **69B**, 1163 (1936).

(9) R. D. Barry, F. Kraft, P. K. Besch, D. J. Watson, and M. Pflaumer, *Steroids*, **2**, 379 (1963).