Anal. Calcd for $C_{14}H_{21}NO_3S$: C, 59.36; H, 7.47; N, 4.94; S, 11.31. Found: C, 59.33; H, 7.41; N, 4.84; S, 11.17.

Acylation of **6a** with acetyl chloride was attempted under a variety of standard conditions but all experiments led to recovery of **6a** in high yield. Under more drastic conditions extensive decomposition of **6a** was observed. Steric approach to nitrogen is apparently strongly hindered because of the neopentyl-like position. NOE: on a degassed 0.2 *M* solution of **6a** in $CDCl_3$.

***N-tert*-Butyl-*O*-2-*p*-tolylsulfonyl-1-phenylethenylhydroxylamine (6b)**: yield 32%, mp 152–154°, nmr ($CDCl_3$) δ 1.17 (s, 9 H, *tert*-butyl), 2.38 (s, 3 H, aryl CH_3), 5.63 (s, 1 H, NH), 6.83 (s, 1 H, vinyl H), ~7.20–8.00 ppm (m, 9 H, aryl protons); ir (KBr) 3255, 3085, 1620, 1590, 1365, 1295, 1285, 1127 cm^{-1}.

Anal. Calcd for $C_{19}H_{23}NO_3S$: C, 66.06; H, 6.71; N, 4.06; S, 9.28. Found: C, 65.98; H, 6.62; N, 3.79; S, 9.20.

Reduction of 6a. Using a procedure similar to that described by Nicolaus, *et al.*,[11] a 91% yield of pure *p*-tolylsulfonylacetone, mp 50.5–51.5° (lit.[19] mp 52°), was obtained. The spectral data were in accordance with the structure. *tert*-Butylamine was detected in the reaction mixture by glc comparison with an authentic sample.

Esr Experiments. A 0.05 *M* solution of dibenzoyl peroxide in benzene was mixed with an equimolar solution of **4a** or **4b** in benzene, and the mixture was degassed. After 5 min, the esr spectrum of the spin adduct was recorded: **5a**, a_N = 14.7 G, a_H = 2.8 G (1 H); **5b**, a_N = 14.5 G, a_H = 4.0 (1 H), 6.0 G (1 H).

Acknowledgment. We are indebted to Dr. J. H. Wieringa for performing the NOE experiments.

Registry No.—**1a**, 13894-21-8; **1b**, 14027-53-3; **1c**, 24378-05-0; **2a**, 16649-50-6; **2b**, 2211-64-5; **4a**, 51869-11-5; **4b**, 51869-12-6; **4c**, 51869-13-7; **5a**, 51869-14-8; **5b**, 51869-15-9; **6a**, 51869-50-2; **6b**, 51869-16-0.

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(2) W. E. Truce and D. G. Brady, *J. Org. Chem.*, **31**, 3543 (1966).

(3) C. J. M. Stirling, *J. Chem. Soc.*, 5863 (1964).

(4) C. H. McMullen and C. J. M. Stirling, *J. Chem. Soc. B*, 1217 (1966).

(5) The sharp melting points and the nmr spectra of **4a,b** point to the presence of only one geometrical isomer. Configurational isomerization is expected to be slow at 37°: T. S. Dobashi, M. H. Goodrow, and E. J. Grubbs, *J. Org. Chem.*, **38**, 4440 (1973).

(6) E. G. Janzen, *Accounts Chem. Res.*, **4**, 31 (1971), and references cited therein.

(7) The usual preference for nitrogen as the nucleophilic site in N-monosubstituted hydroxylamines is well documented: B. Zeeh and H. Metzger in Houben-Weyl, "Methoden der Organischen Chemie," Vol. X-1, Georg Thieme Verlag, Stuttgart, 1971, p 1091.

(8) There is only a very limited amount of literature on the addition of hydroxylamines to any sort of carbon–carbon triple bond: (a) E. Huntress, T. E. Lesslie, and W. M. Hearon, *J. Amer. Chem. Soc.*, **78**, 419 (1956); (b) W. C. Agosta, *J. Org. Chem.*, **26**, 1724 (1961); (c) E. Winterfeldt and W. Krohn, *Chem. Ber.*, **102**, 2336, 2346, (1969); (d) F. de Sarlo, G. Dini, and P. Lacrimini, *J. Chem. Soc. C*, 86 (1971); (e) T. Sheradsky and S. Lewinter, *Tetrahedron Lett.*, 3941 (1972).

(9) It is highly unlikely that the observed peak is due to an OH stretch shifted to lower frequency as a result of hydrogen bonding. To test for intermolecular H bonding, ir spectra were taken at concentrations as low as 10^{-2} mol $l.^{-1}$ but no free OH stretch could be detected. The frequency of the absorption is too low to be the result of intramolecular H bonding of OH in a structure like **3** to a weak H-bond acceptor moiety like the sulfonyl group; see J. W. Dallinga and J. B. F. N. Engberts, *Spectrochim. Acta*, in press.

(10) (a) G. Rawson and J. B. F. N. Engberts, *Tetrahedron*, **26**, 5653 (1970); (b) M. Davies and N. A. Spiers, *J. Chem. Soc.*, 3971 (1959).

(11) O–N bond cleavage upon hydrogenation of *O*-alkylhydroxylamines is a well-known reaction: B. J. R. Nicolaus, P. Pagin, and E. Testa, *Helv. Chim. Acta*, **45**, 358 (1962).

(12) Hydroxylamines containing an unsubstituted OH group give a positive test with Fehling's reagent; see ref 7.

(13) Attempts to isomerize **6a** into the isomeric nitrone by heating in toluene either with or without *p*-toluenesulfonic acid as a possible catalyst were unsuccessful and only led to decomposition.

(14) J. H. Noggle and R. E. Schirmer, "The Nuclear Overhauser Effect," Academic Press, New York, N. Y., 1971.

(15) One could imagine that the barrier to rotation around the carbon–carbon double bond in **6a** is substantially lowered owing to resonance interaction involving partial electron pair localization at α-sulfonyl carbon. However, nmr spectra of **6a** taken in CS_2 down to −110° did not show any splitting of the appropriate signals.

(16) See, for instance, R. Rowan, III, A. Warshel, B. D. Sykes, and M. Karplus, *Biochemistry*, **13**, 970 (1974), and references cited therein.

(17) N,N-Disubstituted hydroxylamines occasionally add through oxygen attack; see ref 7.

(18) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. II, W. A. Benjamin, New York, N. Y., 1966, p 10.

(19) J. Tröger and O. Beck, *J. Prakt. Chem.*, **87**, 289 (1913).

Thermal Rearrangement of Deltacycline to Indan. A Facile and Deep-Seated Aromatization

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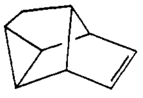
We have been investigating the mass spectral behavior of deltacyclene (tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]non-8-ene, **1**)[1] and a series of related compounds and have observed very strong peaks at *m/e* 118 and 117 in the mass spectra of many of these molecules, especially deltacyclene itself and its thermal precursor, the head-to-side norbornadiene dimer (**2**).[1b,c] This mass spectral pattern is suggestive of the aromatic C_9H_{10} isomer indan (**3**) under similar conditions[2] and indicates that deltacyclene rearranges upon electron impact to indan, which then loses hydrogen in apparent analogy with the mass spectral rearrangement of toluene to the tropylium ion.[3] Since deltacyclene is formed from dimer **2** *via* pyrolysis at ~480°,[1] the mass spectrum of **2** first of all indicates that the analogous fragmentation (a retro Diels–Alder reaction) apparently occurs in the mass spectrometer and, secondly, raises the possibility that deltacyclene might undergo pyrolysis to indan.



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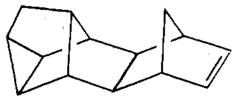

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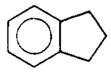

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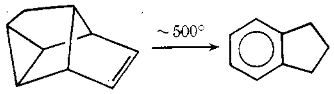
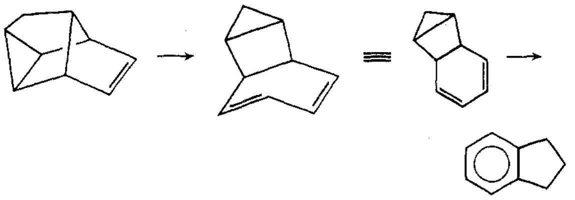
Accordingly, deltacyclene was pyrolyzed at temperatures between 480 and 510°. This resulted in a strikingly clean aromatization to indan (eq 1).



(1)

A number of side products, most with molecular weights of 118, were also formed, but their total concentration was low. In a typical experiment, deltacyclene vapor, mixed with dry nitrogen, was pyrolyzed in a flow system by passing a stream of nitrogen over a reservoir of starting material, passing the mixture through a heated Pyrex tube, and then trapping the products at Dry Ice or liquid nitrogen temperatures. Product mixtures were initially analyzed on a gas chromatograph–mass spectrometer combination, and indan was confirmed as the major product by comparing the mass spectrum, gas chromatographic retention times, and nmr spectrum of the product with the corresponding data for commercial indan. All were indistinguishable. When the mixture was analyzed on SE-30 or FFAP columns at least eight products could be detected, but unreacted deltacyclene (16%) and indan (70%) were by far the major components, with the next most plentiful product (also *m/e* 118) having a concentration of 8% (percentages are based on total volatile product; see Experimental Section). When the dimer **2** was pyrolyzed at temperatures higher than 480° and, especially, with larger contact times, the product mixture contained increasing amounts of indan presumably formed *via* secondary pyrolysis of deltacyclene; this system (**2** → **3**) actually constitutes a fairly good synthesis of indan.

The deltacyclene → indan transformation is reminiscent of the thermal conversion of norbornadiene to toluene, which has been postulated to occur *via* initial formation of cycloheptatriene.[4] The analogous pathway in this system, however, appears to require intolerable strain, and the most straightforward rationalization appears to involve a sequence such as that shown in eq 2.


(2)

This process requires the breaking of two carbon–carbon single bonds in addition to two hydrogen migrations, and the high conversions and low production of side products are somewhat surprising in this context. An interesting *a priori* alternative pathway, the thermally allowed[5] retro homo-Diels–Alder reaction to yield acetylene and bicyclo[2.2.1]heptadiene, is at best a minor process in this pyrolysis, even though it is apparently important in the electron impact reactions of some closely related molecules.[2]

The mechanism of the rearrangement of deltacyclene to indan is under investigation in conjunction with our study of mass spectral behavior of this series of compounds; details will be furnished in a later report.

Experimental Section

Materials. The norbornadiene dimer (hexacyclo[9.2.1.$0^{2,10}$.$0^{3,8}$.$0^{4,6}$.$0^{5,9}$]tetradec-12-ene, **2**) and deltacyclene were prepared according to published procedures.[1] Indan was purchased from Aldrich Chemical Co.

Pyrolyses. The pyrolysis of dimer **2** was carried out in an apparatus essentially the same as that described by Katz[1b,c] and by Cannell,[1a] consisting of a vertical Pyrex tube, 2.5 cm × 1 m, packed with sections of Pyrex tubing and wrapped with heating tape. The reactant was dropped into this tube from a pressure-compensated addition funnel, and the product mixture was collected in a cold trap at the bottom of the tube. A steady flow of nitrogen was maintained during the reaction. Temperatures were measured inside the apparatus with calibrated thermocouples.

Gas-phase pyrolyses were conducted in a generally similar apparatus but with a small pyrolysis tube (10 mm × 25 cm) held in a horizontal position. An inlet reservoir was arranged to allow dry nitrogen to pass directly over a small amount of liquid reactant. The concentration of reactant in the vapor mixture was controlled by cooling or warming the reservoir. The outlet was connected directly to a cold trap which was protected by a Nujol bubbler and a drying tube. After reaction, the product mixtures were warmed to room temperature and samples were injected directly into a flame-ionization gas chromatograph. For experiments with very dilute vapor, the small amount of product was generally dissolved in ether prior to gc analysis.

Preparative pyrolyses of deltacyclene were performed in the large-scale vertical apparatus and the major product was isolated by preparative gas chromatography; the product from the high-temperature, longer contact time pyrolysis of dimer **2** was isolated by fractional distillation. In both cases, the product was identical in all respects with commercial indan.

In the preparative pyrolyses, the product mixture was typically a dark brown liquid which was separable into about 80% indan and 20% viscous, high-boiling polymer. Material balances were generally in the range of 80–90%, which corresponded to yields of indan of 65–75%. In the vapor-phase pyrolyses, the total amounts of material involved were very small (of the order of a few milligrams); so material balances were difficult to determine. The product mixtures, however, appeared to contain much less polymeric material than those in the preparative liquid pyrolyses; so material balances in these systems were probably at least as high as in the preparative reactions.

Preparative gas chromatography was done on a Varian Aerograph 90-P thermal conductivity instrument using a 5 ft × 0.25 in. stainless steel column packed with 15% SE-30 on 60/80 Chromosorb W. Analytical gas chromatography was done on a Perkin-Elmer 990 flame-ionization instrument using 10 ft × 0.125 in. aluminum columns packed with 3–5% SE-30 or FFAP on 80/100 Chromosorb W.

Acknowledgment. This research was supported by grants from the Research Corporation and from the Boston University Graduate School. The mass spectrometer was purchased through a grant from the National Science Foundation.

Registry No.—**1**, 7785-10-6; **2**, 7781-74-0; **3**, 496-11-7.

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Tetrabutylammonium Fluoride. A New Reagent for the Synthesis of Hydantoins

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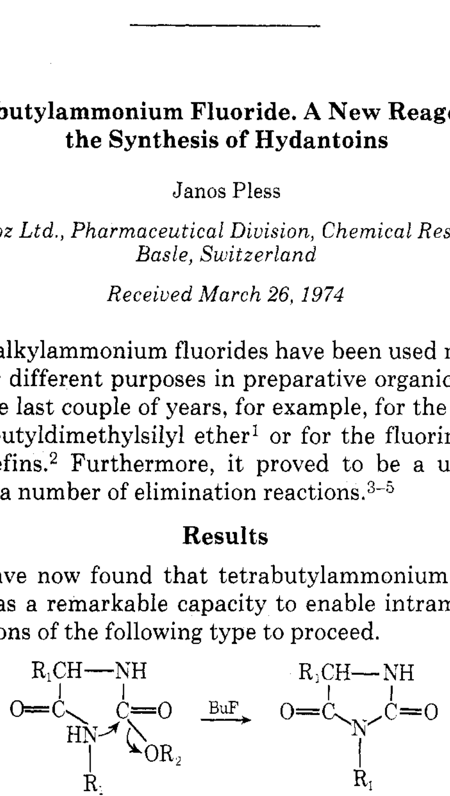
Tetraalkylammonium fluorides have been used more and more for different purposes in preparative organic chemistry in the last couple of years, for example, for the cleavage of *tert*-butyldimethylsilyl ether[1] or for the fluorination of fluoroolefins.[2] Furthermore, it proved to be a useful reagent in a number of elimination reactions.[3-5]

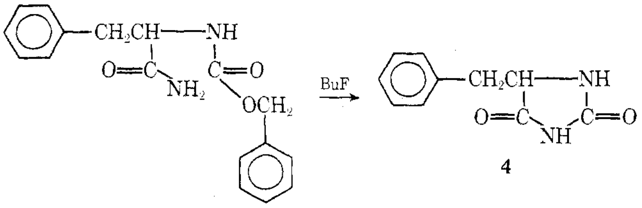
Results

We have now found that tetrabutylammonium fluoride (BuF) has a remarkable capacity to enable intramolecular cyclizations of the following type to proceed.


1 **2**

$R_1 = H, CH_3, C_6H_5CH_2$
$R_2 = CH_3, C_6H_5CH_2$

Thus in boiling tetrahydrofuran carbobenzoxyphenylalaninamide gives the corresponding hydantoin in over 90% yield.


3 **4**

The same reaction could be performed with a series of carbamates to produce substituted hydantoins in excellent yields. Extending this reaction to peptides we found that, *e.g.*, carbobenzoxydipeptides like Z-Leu-Gly-OEt, if exposed to BuF in THF, undergo cyclization with similar ease.