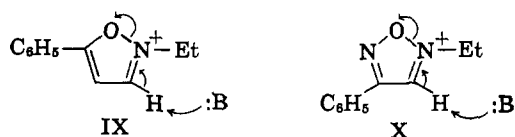


salt (V) where only one of the two positively charged nitrogens is  $\alpha$  to the forming carbanion.

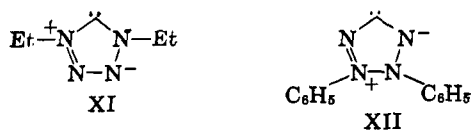
A much more striking result is the rate enhancement derived from adding extra electronegative atoms to the imidazolium ring. Addition of two nitrogen atoms, which gives the tetrazolium salt (VII), increases the exchange rate by a factor of  $2 \times 10^9$ . VII undergoes rapid *base-catalyzed* exchange in 2 *N* DCl at room temperature. If this is a simple inductive effect, it is one of the most powerful inductive effects known. Our preliminary observation that a number of triazolium salts (of widely varied structure) undergo base-catalyzed deuterium incorporation at intermediate acidities (pH 5 to 8)<sup>4</sup> is also in accord with these results. A parallel rate effect is found when one compares the rates of base-induced ring scission of isoxazolium salts (IX) and furazanum salts (X). IX and X react at comparable rates at pH 4<sup>5</sup> and 3.25 *N* HClO<sub>4</sub>,<sup>6</sup> respectively. In these compounds loss of the labile proton



is the rate-determining step so the presence of a discrete ylidic intermediate cannot be demonstrated.

These results prompted us to investigate deuterium incorporation into a position  $\beta$  to the formal positive charge. We believed we might be able to accomplish this by capitalizing on the great accelerating effect of added electronegative atoms, and the compound we chose to study was the 2,3-diphenyltetrazolium salt (VIII). As predicted, this compound does undergo deuterium exchange and at a rate essentially the same as that of the imidazolium salt (VI), a compound in which one is able to place the positive charge (using classical octet resonance structures) on the nitrogens next to the forming anion in the usual manner. The intervening zwitterionic intermediate from VIII violates the very definition of ylide which requires the plus and minus charges to be on adjacent atoms.

It should be noted that in both tetrazolium salts, VII and VIII, the effect of the additional nitrogen atoms may be more than purely inductive. The carbene forms of the zwitterions (structures of type III) have a new possibility for resonance in which the negative charge can be placed on the electronegative element (*cf.* XI and XII), and this would tend to favor ionization<sup>1a</sup> (though this effect is probably not very important). We are continuing our study of these



exchange reactions in the hope of better understanding and separating these effects.

Finally it is of interest to note that the tetrazolium salt (VII) undergoes ring cleavage under more basic conditions to yield nitrogen and diethylcarbodiimide.

(4) R. A. Olofson and W. R. Thompson, unpublished results.

(5) R. B. Woodward and R. A. Olofson, *J. Am. Chem. Soc.*, **83**, 1007 (1961).

(6) R. A. Olofson and J. S. Michelman, *ibid.*, **86**, 1863 (1964).

These reactions are general for 1,4-disubstituted tetrazolium salts and constitute a general method for generating carbodiimides (and a very useful method for generating very reactive carbodiimides) cleanly and quantitatively *in situ*. We shall soon report the applications of these tetrazolium salts as peptide forming reagents.

(7) National Institutes of Health Predoctoral Fellow, 1962-1964.

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### Stereospecific Synthesis of Tricyclo[7.1.0.0<sup>5,7</sup>]decan-3-ol<sup>1</sup>

Sir:

According to a previous discussion,<sup>2</sup> the pentahomocyclopentadienyl system is of considerable interest in connection with the phenomena of homoconjugation and homoaromaticity. We now report a stereospecific synthesis of the parent alcohol, and in the accompanying communication<sup>3</sup> we outline the behavior of the corresponding carbonium ion intermediate in acetolysis of the toluenesulfonate.

The parent alcohol V with the proper configuration and spacing of cyclopropane rings and functional group around an inside eight-membered ring was obtained by the series of reactions, I  $\rightarrow$  V. Epoxidation of 1,3,6-cyclooctatriene (I) with 30% hydrogen peroxide and acetonitrile<sup>4</sup> in methanol gave rise to a monoepoxide fraction containing the isomers II and III in *ca.* equal proportions.<sup>5</sup> The desired isomer<sup>6</sup> II was isolated by preparative vapor phase chromatography<sup>7</sup> (v.p.c.). Its structure was clear from its infrared and n.m.r. spectra. A very distinctive difference between II and III is the presence of an allylic epoxide proton signal at  $\tau$  6.5 in isomer II, whereas the two epoxide proton signal for isomer III occurs at  $\tau$  7.1.

Lithium aluminum hydride reduction of epoxide II in tetrahydrofuran proceeded exclusively at the allylic position<sup>8</sup> to yield dienol<sup>6</sup> IV. The product was homogeneous in v.p.c. on several columns and displayed an appropriate infrared spectrum. Its n.m.r. spectrum displayed signals for four vinyl protons, a proton  $\alpha$  to the hydroxyl group, two bisallylic protons, and four allylic protons at  $\tau$  4.39 (complex multiplet), 6.21 (pentuplet), 7.19 (triplet), and 7.64 (triplet), respectively.

(1) (a) Research sponsored by the U. S. Army Research Office (Durham).

(b) Research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) (a) S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **81**, 6524 (1959); (b) *ibid.*, **83**, 3235, 3244 (1961).

(3) S. Winstein, P. Bruck, P. Radlick, and R. Baker, *ibid.*, **86**, 1867 (1964).

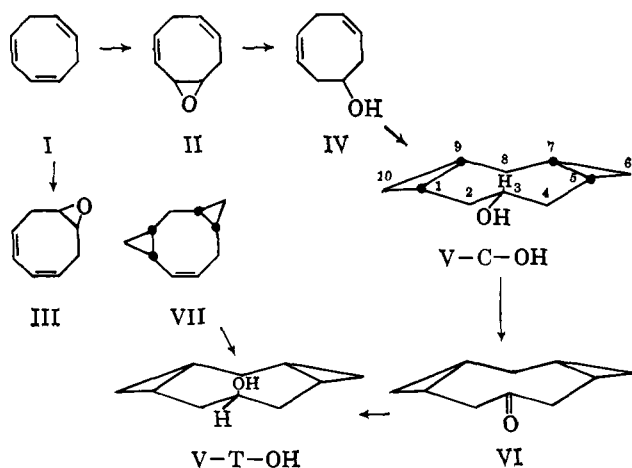
(4) G. Payne, *Tetrahedron*, **18**, 763 (1962).

(5) From epoxidation with perbenzoic acid in benzene, the monoepoxide fraction contains only 20% of II. We are indebted to M. Mousseron of the University of Montpellier, Montpellier, France, for the information that, with myrcene, the use of hydrogen peroxide and acetonitrile instead of monoporphthalic acid shifts the predominant position of monoepoxidation from the trisubstituted olefinic group to one of the two conjugated olefinic groups. This difference in selectivity between ordinary peracids and hydrogen peroxide-acetonitrile may have wide application.

(6) Satisfactory carbon and hydrogen analyses were obtained for the new compounds here mentioned.

(7) An XF-1150 silicone nitrile on Chromosorb W column was employed.

(8) A. Cope and P. Peterson, *J. Am. Chem. Soc.*, **81**, 1643 (1959).



As we had reasons to hope,<sup>2b</sup> reaction on the diene IV with 3 moles of methylene iodide and excess zinc-copper couple proceeded stereospecifically to introduce two cyclopropane rings *cis* to each other and to the hydroxyl group.<sup>9</sup> Conversions of IV to bisadduct up to 90% were observed. The bisadduct fraction was homogeneous in v.p.c. and could be isolated by preparative v.p.c.<sup>7</sup> Alternatively, it can be freed from unsaturated starting material and monoadduct by extracting a pentane solution with saturated aqueous silver nitrate, after which it crystallizes readily. After purification through the *p*-nitrobenzoate,<sup>6</sup> m.p. 124.8–125.4°, the tricyclo[7.1.0.0<sup>6,7</sup>]decan-3-ol<sup>6</sup> V-C-OH had m.p. 57–58°, m.p. of the *p*-toluenesulfonate<sup>6</sup> 104–105°. The epimer of alcohol V-C-OH was obtained by chromic anhydride oxidation to the ketone<sup>6</sup> VI, m.p. 51.5–52.5°, and reduction of the latter with sodium borohydride in methanol. The reduction product consisted of epimeric alcohol to the extent of *ca.* 97%. The isolated epimer,<sup>6</sup> V-T-OH, had m.p. 56–57°, m.p. of the *p*-toluenesulfonate<sup>6</sup> 70–71°. The structure and configuration of the epimeric V-OH alcohols are clear from the spectroscopic and chemical evidence.

The epimeric V-T-OH and V-C-OH display nearly identical n.m.r. spectra, with the triplet signal for the  $\alpha$ -proton on C-3 in V-T-OH at lower field and sharper than in V-C-OH. While the n.m.r. spectra of the alcohols suggest a *cis* arrangement of cyclopropane rings, there is also a compelling stereochemical argument that the cyclopropane rings cannot be *trans* to each other. With a *trans* arrangement of cyclopropane rings, only one alcohol, a *dl*-racemate, would be possible, instead of an epimeric pair. Oxidation of the alcohol to the ketone and subsequent reduction would simply regenerate the same alcohol.

The available evidence shows that in V-C-OH the hydroxyl group is indeed *cis* to the cyclopropane rings, and in V-T-OH it is *trans*. Examination of models suggests a preferred crown-like conformation for tricyclo[7.1.0.0<sup>6,7</sup>]decane systems like V-C-OH and V-T-OH, a substituent on C-3 being either "equatorial" or "axial." That V-C-OH has an equatorial *cis* hydroxyl group and V-T-OH has an axial *trans* hydroxyl is clear from comparison of the n.m.r. C-3 proton signals<sup>10</sup> for the two alcohols, the shorter v.p.c. retention time

(9) For comparison, 1,4-cyclooctadiene yields a 66:34 *cis-trans* mixture of the parent tricyclo[7.1.0.0<sup>6,7</sup>]decane.

(10) (a) R. Lemieux, *et al.*, *J. Am. Chem. Soc.*, **80**, 6098 (1958); (b) A. Cope, S. Moon, and C. H. Park, *ibid.*, **84**, 4843, 4852 (1962).

of V-T-OH on polar columns, and the predominant formation of V-T-OH from "steric approach control" sodium borohydride reduction of ketone VI.

Another route to V-T-OH is hydroboration-oxidation of the 1,3,6-cyclooctatriene bismethylene adduct VII with *cis* cyclopropane rings. This alcohol and its C-2 hydroxyl isomer arise in *ca.* equal proportions from this reaction.<sup>11</sup>

**Acknowledgment.**—We are indebted to Dr. F. Ebel of the Badische Anilin und Soda Fabrikwerke in Ludwigshafen, Germany, for generous supplies of the necessary cyclooctatetraene starting material which made this work possible.

(11) J. Zirner and P. Bruck, unpublished work.

(12) U. S. Rubber Company Foundation Postgraduate Fellow in Physical and Engineering Science for 1961–1962.

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RECEIVED MARCH 6, 1964

### Three-Center Nonclassical Cation in the Pentahomocyclopentadienyl System<sup>1</sup>

Sir:

Since the parent alcohols I-C-OH and I-T-OH in the pentahomocyclopentadienyl system are now available,<sup>2</sup> it is possible to examine the behavior of this system from the viewpoints of homoconjugation and homoaromaticity.<sup>3,4</sup> This report concerns the corresponding carbonium ion intermediate in acetolysis of the toluenesulfonate,<sup>5</sup> I-C-OTs.



I-C-OH



I-T-OH

For acetolysis of I-C-OTs it is possible to make an *a priori* prediction of the kind of delocalized cation to be expected. In a cyclopentadienyl species, electron delocalization must almost inevitably be over all five centers due to the rigid planar geometry, whereas the more flexible and adaptable pentahomocyclopentadienyl species present more possible patterns of electron delocalization. For the cation from I-C-OTs we should consider both three- and five-center nonclassical species such as bishomoallyl,<sup>3,4</sup> trishomocyclopropenyl,<sup>3,4</sup> tetrahomopentadienyl,<sup>4</sup> and pentahomocyclopentadienyl<sup>3</sup> types A, B, C, and D, respectively. Neglecting strain energies involved in reorganizing the carbon skeleton, the corresponding Hückel LCAO-MO delocalization energies in units of  $\beta_1$ , the pertinent resonance integral, are 0.824, 2.000, 1.464, and 1.236, respectively.<sup>6</sup>

(1) (a) Research sponsored by the U. S. Army Research Office (Durham). (b) Research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) P. Radlick and S. Winstein, *J. Am. Chem. Soc.*, **86**, 1866 (1964).

(3) (a) S. Winstein and J. Sonnenberg, *ibid.*, **81**, 6524 (1959); (b) *ibid.*, **83**, 3235, 3244 (1961).

(4) R. J. Piccolini and S. Winstein, *Tetrahedron Suppl.*, **No. 2**, 423 (1963).

(5) While the corresponding carbanion is of even greater interest, good routes to this species are still under investigation.

(6) For contrast, the corresponding delocalization energies for the anions are 0.824, 0.000, 1.464, and 2.472, respectively.