O_4F_2 is only slightly soluble in liquid O_2 (pale brown solution) at 77°K., and the solubility is of the same order of magnitude as that of O_3F_2 (= 0.05 mole %).

Thus the above evidence indicates that a fourth member should be added to the oxygen fluorides known, *i.e.*, OF_2, O_2F_2 and O_3F_2. Since the name oxozone has been used to denote O_4, O_4F_2 may be called *oxozone fluoride*.

The bond strength of the "colored" -O-O- bond, as it occurs in the colored oxygen fluorides and the -O-F bond can be estimated, assuming an atomic chain structure in FOOF and FOOOF, and since the heats of formation of O_3F_2 and O_2F_2 have been determined.[2,3] They are: -O-O- = 61 kcal., -O-F = 50 kcal.

In contrast, the colorless or single -O-O- bond, as in H_2O_2, $(CH_3)_2O_2$, etc., equals 35 kcal., the double bond, O=O = 117 kcal. and the O-O bond in the O_3 mol. = 71 kcal. Actually, of course, besides a chain structure, other, including resonating and radical-like structures, could coexist, particularly in view of the low temperatures involved.

The fact that the "colored" -O-O- and the -O-F bonds are nearly equal may account for the ready substitution of an O-F bond by an O-O bond in oxygen fluorides. Thus one may expect to obtain, under still milder reaction conditions (for example, at 30-50°K.), the higher members O_5F_2 and O_6F_2. Again, in view of the easy "convertibility" of O-F bonds a cyclic O_5 or O_6 polymer, *i.e.*, a new form of oxygen, may be capable of existence.

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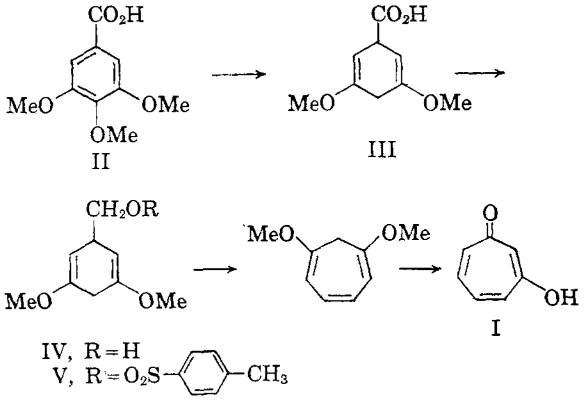
RECEIVED DECEMBER 23, 1960

A NEW APPROACH TO THE SYNTHESIS OF TROPONOID COMPOUNDS: A CONVENIENT SYNTHESIS OF β-TROPOLONE

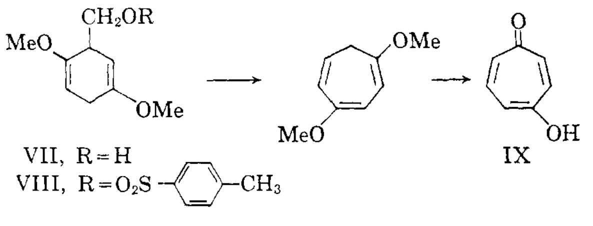
Sir:

The synthesis of troponoid compounds remains a challenging problem. Although many individual syntheses have been recorded, few are of general utility, and many troponoid compounds of real chemical interest have received only cursory study because of the inadequacy of existing synthetic methods. Prominent among the compounds in this category is β-tropolone (I). The difficulties inherent in the synthesis of β-tropolone[1] have kept (I) from assuming its proper place in the comparative study of the chemical, physical and biological properties of the simple tropolones. We now wish to report a method of synthesis of β-tropolone of real practical value and considerable theoretical interest. The method, based on the ring expansion of 1,4-dihydrobenzyl alcohols observed by Nelson,[2] is of considerable generality and has been applied to the synthesis of 1,3-dimethoxycycloheptatriene, 1,4-dimethoxycycloheptatriene, monomethoxycycloheptatriene, β-tropolone, γ-tropolone and tropone.

Birch reduction of 3,4,5-trimethoxybenzoic acid (II) gives 3,5-dimethoxy-1,4-dihydrobenzoic acid (III).[3] Lithium aluminum hydride reduction of III gives the alcohol IV (b.p. 93-95° (0.2 mm.); C, 63.82; H, 8.38). Treatment of IV with *p*-toluenesulfonyl chloride and pyridine at 0° gives an extremely unstable tosylate (V, m.p. 66-67°) in quantitative yield. Solvolysis of the tosylate V in refluxing pyridine gives a mixture of 1,3-dimethoxycycloheptatrienes ($\lambda_{\max}^{\text{EtOH}}$ 288 $m\mu$; C, 71.10; H, 7.54). Oxidation of the mixture of 1,3-dimethoxycycloheptatrienes with bromine using the procedure of Johnson[1] gives β-tropolone in 70-80% yield. β-Tropolone (m.p. 183-183.5°) thus prepared shows $\lambda_{\max}^{\text{EtOH}}$ 247, 254, 270, 297 and 307 $m\mu$ $\lambda_{\max}^{0.1\text{N NaOH}}$ 256, 266, 294 and 304 $m\mu$; C, 68.71; H, 4.97; and gives a picrate, m.p. 166-167°, in accord with the literature.[1] This procedure is quite suitable for preparation of β-tropolone on a relatively large scale. Solvolysis of 145 g. of the tosylate V in refluxing pyridine for three minutes gives 51.6 g. (76%) of the mixture of 1,3-dimethoxycycloheptatrienes. Oxidation of 25.6 g. of the 1,3-dimethoxycycloheptatriene gives 16.5 g. (81%) of β-tropolone. The over-all yield of β-tropolone from 3,4,5-trimethoxybenzoic acid averaged about 28% in four runs.



Birch reduction of 2,5-dimethoxybenzoic acid (VI) then lithium aluminum hydride reduction of the crude dihydroacid gives the alcohol VII (b.p. 82-83°(0.2 mm.); C, 63.71; H, 8.55). Tosylation and solvolysis of the tosylate (VIII) in refluxing pyridine gives a mixture of 1,4-dimethoxycycloheptatrienes (b.p. 90-95° (0.2 mm.; C, 70.84; H, 7.82) which on oxidation with bromine[4] gives γ-tropolone (IX, m.p. 209-211°). Methylation of IX with diazomethane gives γ-tropolone methyl ether identical in infrared and ultraviolet absorption with an authentic sample.[5]



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(1) R. B. Johns, A. W. Johnson and M. Tišler, *J. Chem. Soc.*, 4605 (1954); R. B. Johns and A. W. Johnson, *Chem. and Ind.*, 192 (1954).

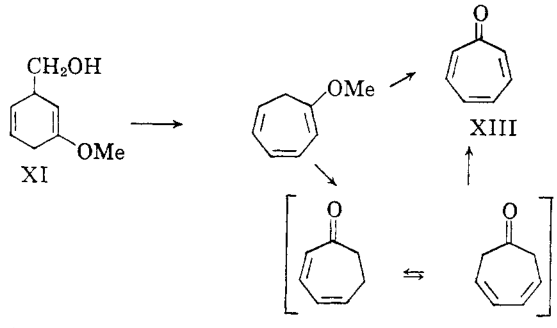
(2) N. A. Nelson, J. H. Fassnacht and J. U. Piper, *J. Am. Chem. Soc.*, **81**, 5009 (1959).

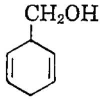
(3) M. E. Kuehne and B. F. Lambert, *ibid.*, **81**, 4278 (1959).

(4) R. S. Coffey, R. B. Johns and A. W. Johnson, *Chem. and Ind.*, 658 (1955); R. S. Coffey and A. W. Johnson, *J. Chem. Soc.*, 1741 (1958).

(5) J. Meinwald and O. L. Chapman, *J. Am. Chem. Soc.*, **80**, 633 (1958).

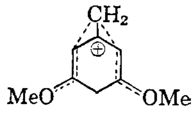
Lithium aluminum hydride reduction of the crude dihydroacid obtained by Birch reduction of 3-methoxybenzoic acid (X) gives 3-methoxy-1,4-dihydrobenzyl alcohol (XI; b.p. 93–96° (0. 2 mm.); C, 68.71; H, 8.83) in modest yield.[6] The n.m.r. spectrum of the alcohol XI shows a two proton peak at 4.41 p.p.m. and a one proton peak at 5.48 p.p.m.[8] For comparison the olefinic protons of 1,4-dihydrobenzyl alcohol (XII) appear as a four proton peak at 4.33 p.p.m., and the olefinic protons of 3,5-dimethoxy-1,4-dihydrobenzyl alcohol (IV) appear as a two proton peak at 5.50 p.p.m. Tosylation of XI and solvolysis in refluxing pyridine gives a mixture of methoxycycloheptatrienes (b.p. 67–70° (20 mm.); $\lambda_{\max}^{\mathrm{EtOH}}$ 289 mμ). Bromine oxidation of the methoxycycloheptatrienes gives in low yield tropone (XIII, $\lambda_{\max}$ 223, 227, 231, 235, 238, 307 mμ). Acid hydrolysis of the mixture of methoxycycloheptatrienes gives a mixture of 2,4- and 3,5-cycloheptadienones[9] (5.90, 6.02, 6.16, and 6.31 μ) which air oxidizes to tropone in somewhat better yield.[10]



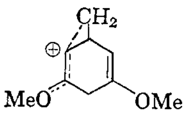


XII

The solvolytic ring expansion of the tosylates of IV, VII and XI is of considerable interest. Contemplation of the possibilities for anchimerically assisted ionization of V suggests either a doubly assisted ionization leading to an ion such as XIV (not necessarily symmetric) or a singly assisted ionization to an ion such as XV.



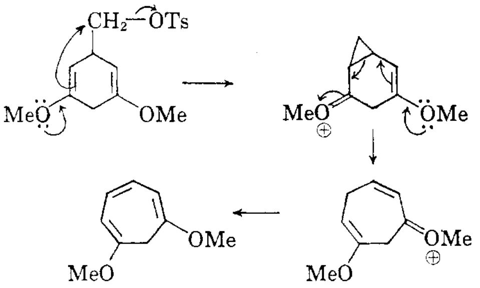
XIV



XV

This mechanistic dichotomy is somewhat analogous to that encountered in the ionization of pentamethyl cyclopentadienylcarbinyl brosylate[11] and tosylate.[12] Comparison of the behavior of 3,5-dimethoxy-1,4-dihydrobenzyl tosylate (V) and 1,4-dihydrobenzyl tosylate in refluxing pyridine strongly suggests the incursion of an assisted ionization which favors ring expansion in the case of V. *In refluxing pyridine the tosylate V (0.62 molar) is completely destroyed in 30 seconds.* In contrast 1,4-dihydrobenzyl tosylate (0.76 molar) is not completely destroyed after one hour in refluxing pyridine, and no cycloheptatriene is obtained in the work up.[13] The principal reaction in this case appears to be alkylation of the pyridine. Attempts to obtain satisfactory solvolysis rates for the tosylates of IV, VII, XI and XII using collidine as solvent are in progress.

It is interesting to note that the ring expansion of V can be considered the mechanistic analog of the peracid oxidation of benzal ketones to enol esters.[14]



Acknowledgment.—This research was supported by grant CY-4253 from the Cancer Division, National Institutes of Health, Public Health Service.

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(6) A by-product which may be derived from the tetrahydroacid reported[4,7] to be the product of Birch reduction of 3-methoxybenzoic acid is also obtained. The formation of XI requires the formation of 3-methoxy-1,4-dihydrobenzoic acid in the Birch reduction of X. The mechanistic significance of this observation will be discussed in the complete report of this investigation.

(7) A. J. Birch, P. Hextall and S. Sternhell, *Aust. J. Chem.*, **7**, 256 (1954).

(8) Tau values relative to internal tetramethylsilane in carbon tetrachloride (G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958)).

(9) J. Meinwald, S. L. Emerman, N. C. Yang and G. Büchi, *J. Am. Chem. Soc.*, **77**, 4401 (1955).

(10) E. E. van Tamelen and G. T. Hildahl, *ibid.*, **78**, 4405 (1956).

(11) L. De Vries, *ibid.*, **82**, 5242 (1960).

(12) S. Winstein and M. Battiste, *ibid.*, **82**, 5244 (1960).

(13) Acetolysis (*ca.* 36 hours at 90°) of 1,4-dihydrobenzyl tosylate gives cycloheptatriene in good yield.[2]

(14) E. Wenkert and M. Rubin, *Nature*, **170**, 708 (1952).

(15) Recipient of a travel grant from the Wellcome Trust.

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RECEIVED DECEMBER 23, 1960

DIRECT RADIATION-INDUCED SYNTHESIS OF IODOBENZENE-I^{131} FOLLOWING FISSION PRODUCT RECOIL INTO BENZENE SOLUTION[1]

Sir:

In the last several years, the excited chemical species created during the dissipation of nuclear energy frequently have been utilized for the direct synthesis of various radioisotopically-labeled molecules.[2] Processes accompanying fission recoil—kinetic energy of recoil, radiation damage to the surroundings, and later the beta decay of the primary fission fragments—furnish abundant opportunity for the formation of excited chemical species which may then react with the incorporation of fission product radioactivity into particular chemical compounds.[3] We have experimentally caused

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(1) This research has been supported by A.E.C. Contract No. AT-(11-1)-407.

(2) See the review by A. P. Wolf in *Ann. Rev. Nuclear Sci.*, **10**, 259 (1960).

(3) Some of the chemical effects of fission fragments have been reviewed by G. N. Walton in Progress in *Nuclear Physics*, **6**, 193 (1957). The reactions of fission fragments recoiling into solid ferrocene and