

9.13 and 8.25 τ ; infrared: $>C=C<$ 8165 cm.^{-1}).^{2,3}

As to the mechanism of the reaction, formation of chlorocarbene from methylene chloride and I is likely to be the first step.⁴ As a strongly nucleophilic reagent, I can be visualized to combine with the carbene by either of two ways: path (a) assumes electrophilic addition of the carbene to the π -electrons of the double bond, generating intermediate II which gives V *via* β -elimination. Or, the carbene may attack the incipient vinylcarbanion to form intermediate III, (path b), which generates vinylcarbene IV by α -elimination.⁵ Cyclization of the latter by rotation of the *gem* dimethyl group through 90° will lead to the cyclopropene V. The subsequent replacement of the olefinic proton in V by lithium occurs on reaction with strongly basic I. The resulting cyclopropenyllithium compound VI is also formed when V is allowed to react with methyllithium in tetrahydrofuran at 0°.

This increased acidity of the olefinic proton in cyclopropenes has been predicted from theoretical considerations^{6,7} which attribute a high degree of s-character to the C—H bond because of the large "ring strain." Deuterium exchange work on short-lived cyclopropene intermediates supports this concept.⁷ Additional indication of the correctness of the theory is given by the increased acidity of VII (pK_a 3.7) when compared with other α,β -unsaturated carboxylic acids.

The reaction is being extended at the present time to the introduction of other functional groups in the 1-position of cyclopropenes. A detailed investigation of the mechanism is also in progress.

(2) Other 1,2-dialkyl-substituted cyclopropenes are reported to exhibit C=C stretching vibration in the same region: P. K. Faure and J. C. Smith, *J. Chem. Soc.*, 1818 (1956); W. v. E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960).

(3) It may be of interest to point out the unusually large shift in the C=C stretching frequency (110 cm.^{-1}) of the cyclopropene ring system caused by introduction of a second alkyl substituent on the double bond.

(4) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960).

(5) For the equivalent mechanism of the reaction of chlorocarbene with alkyllithium compounds see: G. L. Closs, Abstracts of Papers of the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960, p. 9-P.

(6) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(7) K. B. Wiberg, R. K. Barnes and J. Albin, *J. Am. Chem. Soc.*, **79**, 4994 (1957).

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A NEW FLUORIDE OF OXYGEN— O_4F_2 ¹

Sir:

The preparation and properties of pure ozone fluoride, or O_3F_2 , were described recently.^{2,3,4} It has now been established that the elusive O_4F_2 ^{2,3} also can be obtained. As in the case of O_2F_2 , and O_3F_2 , it is produced by an electrical discharge at low

(1) This research was financed at first, in part, by the Army Ballistic Missile Agency, Redstone Arsenal, Huntsville, Alabama, and at present by the Department of the Navy, Office of Naval Research.

(2) A. D. Kirshenbaum and A. V. Grosse, *J. Am. Chem. Soc.*, **81**, 1277 (1959), see there for previous literature.

(3) A. D. Kirshenbaum, J. G. Aston and A. V. Grosse, *Final Report*, Contract No. DA-36-034-ORD-2250, Nov. 18, 1958.

(4) A. D. Kirshenbaum, A. V. Grosse and J. G. Aston, *J. Am. Chem. Soc.*, **81**, 6398 (1959).

temperatures and pressures by using a mixture of 2 moles O_2 to 1 mole F_2 , by cooling more effectively and to lower temperatures, *i.e.*, 60–77°K. (instead of 90°K.), and using less power in the discharge (*i.e.*, 4.5–4.8 milliamp at 840–1280 volts as against 20–30 ma. at 2000–3000 v.).

At 77°K. O_4F_2 is a reddish brown *solid*, depositing on the glass walls of the discharge vessel between the electrodes. It differs in color from O_3F_2 , and sometimes forms clusters of long needle-like brown crystals.

O_4F_2 has a vapor pressure of less than 1 mm. at 90°K. It is a liquid and stable, at least for a couple of hours, at 90°K., since no noticeable rise in pressure occurs. Between 90 and 110°K. it decomposes slowly into O_3F_2 and O_2 , and the latter at 110°K. to O_2 and O_2F_2 . Since O_2F_2 in turn forms $O_2 + F_2$ at about 200°K. the whole O_4F_2 is decomposed into O_2 and F_2 gas.

The composition of O_4F_2 was established both by (a) synthesis and (b) analysis. In a synthetic case 355 cm.^3 (at S.T.P.), of a 2.05 \pm 0.03:1 O_2/F_2 mixture reacted at 77°K. in a discharge vessel described previously.^{1,2} The gases were admitted at a rate of 2.0 $\text{cm.}^3/\text{min.}$ (S.T.P.); the pressure was 5–15 mm. and the current 4.5 to 4.8 milliamp. at 840–1280 volts. All of the mixture was converted quantitatively to the solid reaction product, except for 15.4 cm.^3 of gas, which was pumped off periodically in order to keep the gas phase composition constant. Even assuming these 15.4 cm.^3 to be pure O_2 , the composition of the product should equal $O_{4.00}F_{2.06}$.

Typical analyses of the gas produced from the solid product, using a Moissan mercury absorption buret for F_2 and an Orsat apparatus for O_2 , are: 96.9 cm.^3 (at S.T.P.) contained 66.3 mole % O_2 and 33.7 mole % F_2 , ratio $O_2:F_2 = 1.95 \pm 0.03$; 55.6 cm.^3 gas (at S.T.P.) gave 66.5 mole % O_2 and 33.4 mole % F_2 , ratio $O_2:F_2 = 1.98 \pm 0.05\%$. Theoretical for O_4F_2 is 2.00.

The vapor pressures of O_3F_2 , O_2F_2 and O_2 differ widely and any O_2 present can be pumped off easily; thus the elementary composition O_4F_2 cannot be due to dissolved O_2 . The proof that it is *not* due to O_3 is more difficult. This proof is necessary, however, because O_2 gas alone, under the pressure, temperature and discharge conditions, is converted into liquid or solid O_3 . Furthermore, liquid O_3 and liquid O_3F_2 mix homogeneously in any proportion at 90°K., and the $O_3 + 3O_3F_2$ mixture, on cooling to 77°K., forms a brown mass very similar in appearance to O_4F_2 . Attempts to distinguish O_4F_2 from the $O_3 + O_3F_2$ mixtures by visible spectra could not be made because the molecular extinction coefficients for O_3F_2 and O_4F_2 were not known.

It occurred to us that a simple differentiation could be provided by the solubility behavior of the compounds in liquid O_2 . It was found that our samples (0.7–1.0 g.) of O_4F_2 , extracted at 77°K. by condensation of liquid O_2 (≈ 25 cc.), gave no visible trace of O_3 . On analysis this particular sample, after liquid O_2 extraction and pumping off all O_2 , had the composition $O_{4.00}F_{2.04}$. In contrast, the $O_3 + 3O_3F_2$ mixture prepared from pure O_3 and O_3F_2 , immediately gave a deep blue extract of O_3 in O_2 .

O_4F_2 is only slightly soluble in liquid O_2 (pale brown solution) at $77^\circ K.$, 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_8 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 $30-50^\circ K.$), 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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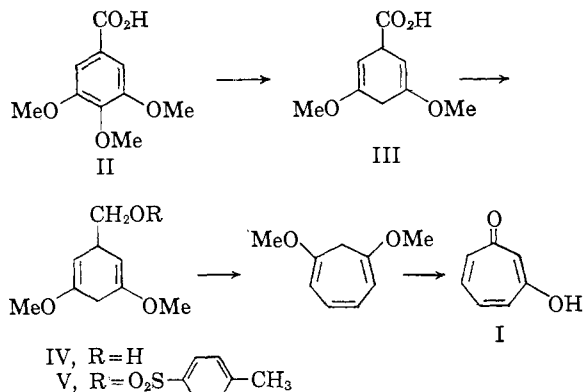
A NEW APPROACH TO THE SYNTHESIS OF TROPONOID COMPOUNDS: A CONVENIENT SYNTHESIS OF β -TROPOLONE

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 -tropolone¹ 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.

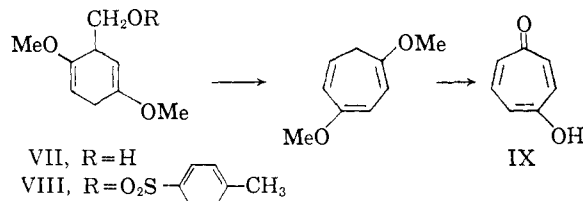
Birch reduction of 3,4,5-trimethoxybenzoic acid (II) gives 3,5-dimethoxy-1,4-dihydrobenzoic acid (III).³ Lithium aluminum hydride reduction of III

gives the alcohol IV (b.p. $93-95^\circ$ (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. $66-67^\circ$) in quantitative yield. Solvolysis of the tosylate V



in refluxing pyridine gives a mixture of 1,3-dimethoxycycloheptatrienes ($\lambda_{\text{max}}^{\text{EtOH}}$ 288 $m\mu$; C, 71.10; H, 7.54). Oxidation of the mixture of 1,3-dimethoxycycloheptatrienes with bromine using the procedure of Johnson¹ gives β -tropolone in 70-80% yield. β -Tropolone (m.p. $183-183.5^\circ$) thus prepared shows $\lambda_{\text{max}}^{\text{EtOH}}$ 247, 254, 270, 297 and 307 $m\mu$, $\lambda_{\text{max}}^{0.1N \text{ NaOH}}$ 256, 266, 294 and 304 $m\mu$; C, 68.71; H, 4.97; and gives a picrate, m.p. $166-167^\circ$, 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. $82-83^\circ$ (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-dimethoxycyclo-



heptatrienes (b.p. $90-95^\circ$ (0.2 mm.); C, 70.84; H, 7.82) which on oxidation with bromine⁴ gives γ -tropolone (IX, m.p. $209-211^\circ$). 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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