methyltestosterone acetate (If acetate) (m.p. 171–173°, $[\alpha]_D$ +44°, $\lambda_{max.}$ 240 mμ, log ε 4.19. Found: C, 77.23; H, 9.81).

While anti-tumor screening of the above described 2-methyl hormones is still in progress, Ia and IIa have already been shown to be very effective tumor inhibitors.

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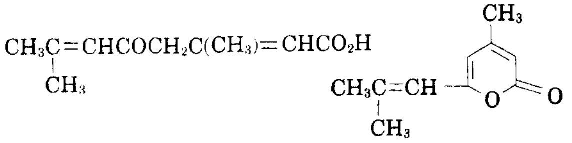
2-Pyrones. XXIII. 4-Methyl-6-(2′-methylpropenyl)-2-pyrone

Sir:

We wish to report the synthesis of a new ten carbon isoprenoid lactone which is of interest as a simple multiple of senecioic acid in studies of the biosynthesis of cholestrol from acetate.[1–7] 4-Methyl-6-(2′-methylpropenyl)-2-pyrone (II), the lactone of the enol form of γ-senecioylsenecioic acid (I) has been prepared by the acylation of β-methylglutaconic anhydride with senecioyl chloride followed by decarboxylative rearrangement. This is a modification of a synthetic route previously described,[8] but successfully applied here for the first time to an aliphatic acid chloride having over four carbon atoms.



$CH_3\underset{CH_3}{C}{=}CHCOCH_2C(CH_3){=}CHCO_2H$

I II

A solution of β-methylglutaconic anhydride in pyridine and ether was treated with senecioyl chloride. Ether extraction of the acidified reaction mixture gave a red oil which was decarboxylated by flash distillation and refractionated to give 12% yield of 4-methyl-6-(2′-methylpropenyl)-2-pyrone, m.p. 46.5–47.5°, (*Anal.* Calc'd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.08; H, 7.37) showing the 2-pyrone carbonyl absorption band at 1730 cm.$^{-1}$ and the trisubstituted ethylenic absorption band at 840 cm.$^{-1}$. Reaction with bromine gave 3-bromo-4-methyl-6-(2′-methyl-2′,3′-dibromopropyl)-2-pyrone, m.p. 119–120°. (*Anal.* Calc'd for $C_{10}H_{11}Br_3O_2$: C, 29.80; H, 2.75. Found: C, 29.88; H, 3.10) showing the 2-pyrone carbonyl absorption band at 1724 cm.$^{-1}$ shifted slightly as with other 3-substituted types.[9]

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Ozonolysis of Phenanthrene in Chloroform

Sir:

Schmitt, Moriconi, and O'Connor[1] recently claimed the preparation of the first stable monomeric ozonide of an aromatic hydrocarbon. The material was obtained by the ozonolysis of phenanthrene in either chloroform or acetic acid. It melted at 65–90°. It was assigned a monoozonide structure on the basis of elementary analyses, a Rast molecular weight determination, catalytic hydrogenation to 2,2′-biphenyldicarboxaldehyde, and infrared spectra which showed strong bands in the region 5.7–5.9 μ, which Briner[2] had originally ascribed to ozonides.

Criegee[3] has shown that pure simple ozonides, such as the monoozonide of phenanthrene would be, do not absorb in the 5.6–6.2 μ region, which is the carbonyl region. Briner[4] has recently acknowledged the findings of Criegee and ascribed his results to the formation of aldehydes or ketones during the passage of ozone through the reaction mixture.

We have ozonized phenanthrene (5.9 g.) in chloroform (60 ml.) at −60° and have immediately precipitated the product (7.3 g., 98% yield, m.p. 129–130°) by addition of either ligroin or methanol. Several recrystallizations from benzene by addition of ligroin gave an 80% recovery of material melting at 139–141° (*Anal.* Calcd. for $C_{14}H_{10}O_3$: C,[5] 74.33; H, 4.46; Active 0, 7.07. Found: C, 74.58; H, 4.80; Active 0, 6.95). The material was

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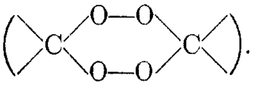
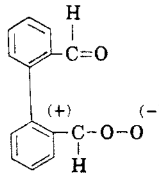
(5) Schmitt, Moriconi, and O'Connor[1] erred in this calculation. Their product, therefore, analyzed 1% low in carbon.

insoluble in ether. Upon reduction with sodium iodide it yielded 2,2′-biphenyldicarboxaldehyde.

Cryoscopic molecular weight determinations of the pure material (monomer value 226) in benzene (1370, 1392), bromoform (1790, 1860), and nitrobenzene (1200) show that the substance is at least a hexamer. It is perhaps of even higher molecular weight since in nitrobenzene the molecular weight decreased in an hour's time to that of a dimer. There is little doubt that at the temperature of a Rast molecular weight determination depolymerization and/or decomposition would occur. The infrared spectrum of the pure substance showed a very weak carbonyl band (5.9 μ). These facts suggest a linear polymer of the zwitterion I (Criegee mechanism)[6] with a carbonyl group at one end and an addition product of the zwitterion group at the other end (structure II). The adding molecule could be a simple one like water or methanol or another zwitterion(I), resulting in a diperoxy linkage .



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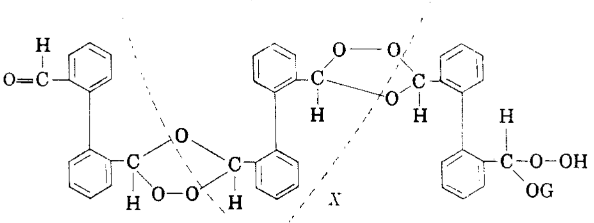

II

Only when the ozonolysis reaction mixture was allowed to stand for a while before precipitation of the product, or when the pure product was redissolved in chloroform for a period of time, was a product similar to that of Schmitt, Moriconi, and O'Connor[1] obtained. These low-melting materials were partially soluble in ether, showed a low active oxygen content, and had strong bands in the carbonyl region of their infrared spectra. It seems apparent that the impure material of Schmitt, Moriconi, and O'Connor was a mixture of the polymeric substance and carbonyl-containing nonperoxidic decomposition products.

The ozonolysis in acetic acid was also repeated. The product appears to be a mixture of the polymer and an acetoxy hydroperoxide. This will be reported upon in a later paper.

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[6] For summary of mechanism see Bailey, *J. Am. Chem. Soc.*, 78, 3811 (1956).