NdCo(CN)$_6$ in water for K increases steadily as c increases. Since the results for LaCo(CN)$_6$ and for[4] LaFe(CN)$_6$ in water do not show this drift, and since Λ_0 is well established, it can only be assumed that the fault is of an experimental nature.

With regard to the plotting procedures of Shedlovsky[2] and the analogous one of Fuoss and Kraus[7], the conclusions drawn may be in error even when using the correct expressions if the measurements are faulty. Accordingly a good check is to calculate K for each measurement and this may be done by use of

$$c_1 = c\Lambda S'(z)/\Lambda_0 = c\Lambda/\Lambda_0 F'(z) \tag{4}$$

where $F'(z)$ is the special Fuoss-Kraus function,[7] together with equations (2) and (3).

Finally, by analogy with the K values of a number of lanthanide sulfates, which also have been evaluated from conductances in water,[8] and which are all around $pK = 3.65$, one would expect to find only small differences among the pKs of the lanthanide cobalticyanides in a given solvent.

(7) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 476 (1933).

(8) F. H. Spedding and S. Jaffe, ibid., **76**, 882 (1954).

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THE REACTION OF PHOSPHORANE DERIVATIVES WITH OZONE. BENZIL-TRIALKYL PHOSPHITE ADDUCTS AND PHOSPHINEACYLMETHYLENES[1]

Sir:

We have described[2] the formation of benzoic anhydride (III, ca. 30%), benzil (V, ca. 67%) and trimethyl phosphate (VI, ca. 94%) in the reaction of oxygen with the crystalline 1:1 adduct (I) derived from benzil and trimethyl phosphite. The reaction was carried out in benzene solution at room temperature, for five days. We wish to report now the rapid conversion of the adduct I into benzoyl peroxide (IV, ca. 50%), benzil (V, ca. 30%) and trimethyl phosphate (VI, nearly quantitative yield) by ozone in hexane solution at $-70°$. Ozone reacted rapidly with the benzil-triphenyl phosphite adduct[2] (II) to give benzoyl peroxide (IV ca. 38%), benzil (V ca. 40%) and triphenyl phosphate (VII).
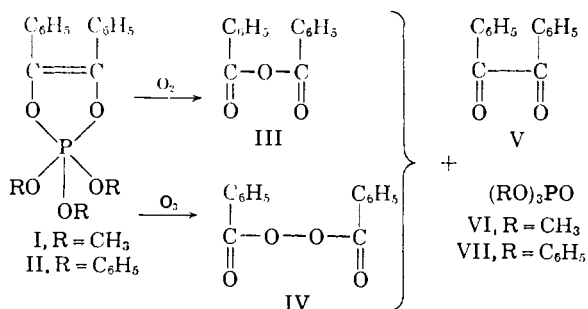
I, R = CH$_3$
II, R = C$_6$H$_5$

III

V

VI, R = CH$_3$
VII, R = C$_6$H$_5$

IV

(2) F. Ramirez, R. B. Mitra and N. B. Desai, THIS JOURNAL, **82**, 2651 (1960).

A second type of phosphorane derivative,[3] the relatively stable triphenylphosphineacylmethylenes (VIII and IX), have been found to react very rapidly with ozone, in methylene chloride at $-70°$. VIII gave benzil (V, 80%), benzoyl peroxide (IV, 14%) and triphenylphosphine oxide (XI, 90%). IX yielded phenylglyoxal (X, 88% as 2,4-dinitrophenylosazone, m.p. 296-298°) and triphenylphosphine oxide (XI, 96%).[4]
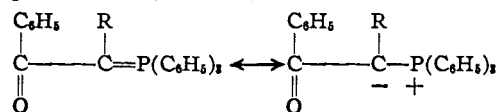

VIII, R = C$_6$H$_5$; IX, R = H

The ratio of benzoyl peroxide (IV) to benzil (V), in the reaction of ozone with adduct I decreases as the polarity of the solvent and the temperature are increased: 37% of IV and 52% of V were formed in methylene chloride at $-70°$. In methylene chloride at room temperature, the yield of IV was 14% and that of V was 60%; in addition, some benzoic anhydride (III, 11%) was obtained under these conditions. Under the conditions of the ozonization, neither adduct (I) nor ylide (VIII) reacted appreciably with pure oxygen[5] or with benzoyl peroxide; benzil was not attacked by ozone.

The reactions with ozone were carried out under anhydrous conditions and the composition of the reaction mixture was ascertained by comparisons of the infrared spectra with those of authentic mixtures. In addition, peroxidic material was determined by the iodimetric method,[6] and all the products were isolated.

We have suggested[2,7] that the "phosphinemethylene secondary ozonide" XII is an intermediate in the reaction of oxygen with the adducts I and II. Possible modes of decomposition of the ozonide XII to: (a) benzoic anhydride plus phosphate ester, or (b) benzil plus a peroxidic phosphate ester XIII are shown below. XIII is the phosphorus analog of Criegee's "zwitterion"[6] and should decompose into molecular oxygen plus a phosphate ester, for instance through dimerization.

XII   XIII
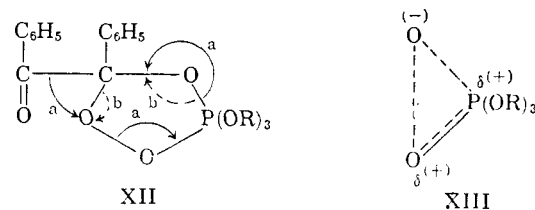
The reaction of the adducts I and II with ozone could involve the "perozonide" XIV (or a five-membered equivalent). Possible decompositions of XIV to: (a) benzoic anhydride[8] plus the peroxidic

(3) F. Ramirez and S. Dershowitz, J. Org. Chem., **22**, 41 (1957); cf. footnote 1.

(4) The formation of olefins from this type of compound and peracetic acid has just been reported (D. B. Denney and L. C. Smith, THIS JOURNAL, **82**, 2396 (1960)).

(5) Some reactive phosphinemethylenes are converted to dimeric olefins by molecular oxygen (H. J. Bestmann, Angew. Chem., **72**, 34 (1960).

(6) P. Bailey, Chem. Revs., **58**, 925 (1958).

(7) F. Ramirez and N. B. Desai, THIS JOURNAL, **82**, 2652 (1960).

(8) For anhydride formation in ozonization see ref. 6, pp. 951 and 964.

phosphate ester XIII (*i.e.*, phosphate + oxygen), or (b) benzil plus molecular oxygen and phosphate ester, are indicated by the arrows.[9] Presumably, the ozonides XII and XIV are derived from a dipolar form of the adducts (IA, IIA).

XIV

IA, IIA
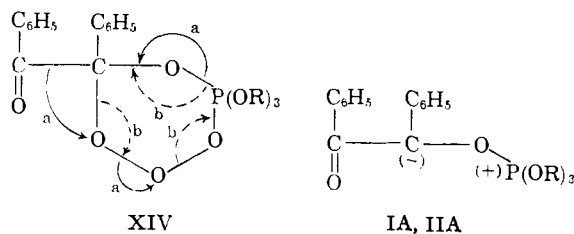
Benzoyl peroxide can be derived from the "primary ozonide" XV formed by attack at the carbon–carbon double bond of the cyclic adduct. A possible path may involve XVI.

XV

XVI
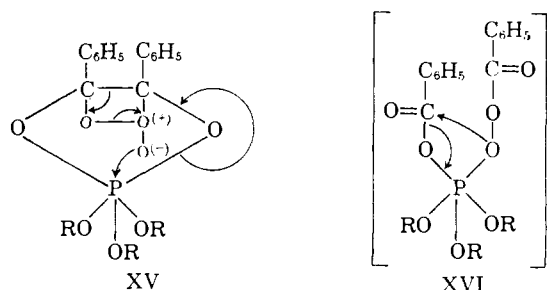
The primary ozonide XVII (or its five-membered equivalent) derived from the phosphinemethylenes (VIII, IX) should collapse to the *alpha*-dicarbonyl compound and a peroxidic phosphine oxide (like XIII).
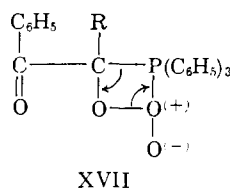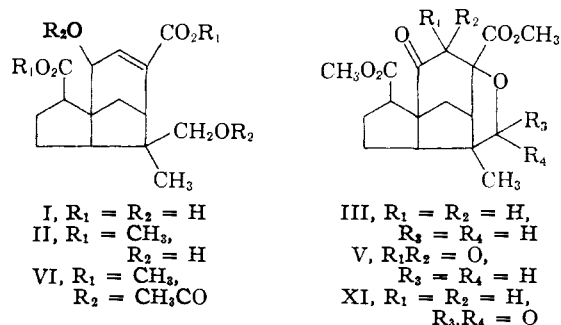
XVII

## SHELLOLIC ACID, A CEDRENOID SESQUITERPENE FROM SHELLAC

Sir:

Shellolic acid is a component of the acid fraction obtained on basic hydrolysis of shellac, a resin of insect origin.[1] We propose that it is a sesquiterpene of structure I with *the rare cedrene skeleton*.[2]

(1) *Cf.*, for example, A. Tschirch and E. Stock, "Die Harze," Vol. II, Borntraeger, Berlin, 1936, p. 1443 *et seq.*; S. C. Sen Gupta, "Report of the Proceedings of the Symposium on Lac and Lac Products," Indian Lac Research Institute, 1956, p. 72.

(2) G. Stork and R. Breslow, THIS JOURNAL, 75, 3291, 3292 (1953); G. Stork and F. H. Clarke, Jr., *ibid.*, 77, 1072 (1955); Pl. A. Plattner, A. Fürst, A. Eschenmoser, W. Keller, H. Kläui, St. Meyer and M. Rosner, *Helv. Chim. Acta*, 36, 1845 (1953). The only other naturally-occurring compound hitherto reported to possess this skeleton is cedrol, an intimate relative of cedrene.

I, $R_1 = R_2 = H$
II, $R_1 = CH_3$, $R_2 = H$
VI, $R_1 = CH_3$, $R_2 = CH_3CO$

III, $R_1 = R_2 = H$, $R_3 = R_4 = H$
V, $R_1R_2 = O$, $R_3 = R_4 = H$
XI, $R_1 = R_2 = H$, $R_3,R_4 = O$

Earlier work[3,4] established that shellolic acid is a compound $C_{13}H_{16}(OH)_2(CO_2H)_2$ containing an ethylenic double bond. The relationship between the functional groups has been elucidated as follows. The spectra of dimethyl shellolate (II), $\lambda_{max}^{CHCl_3}$ 2.9, 5.8–5.9, 6.11 μ, λ_{max}^{EtOH} 230 mμ (ε 6000), show that the double bond is conjugated with a carboxylic ester group. The n.m.r. spectrum (CHCl₃) shows one vinylic hydrogen, which gives a doublet ($J\sim3$ c./s.) with τ = 3.51, and one C–CH₃ group (confirmed by Kuhn–Roth) which gives a singlet with τ = 8.83. Oxidation of II with manganese dioxide gave a dehydro product,[5] III, m.p. 122.5–124°, $\lambda_{max}^{CHCl_3}$ 5.75 (sh), 5.79 and 5.83 (sh) μ, no high intensity ultraviolet absorption >210 mμ. Treatment of II with methanolic sodium methoxide gave, *inter alia*, a product, IV, m.p. 155–156°, $\lambda_{max}^{CHCl_3}$ 5.8 (br) μ, also lacking high intensity ultraviolet absorption. Oxidation of III with selenium dioxide formed an α-diketone V, m.p. 200–203°, $\lambda_{max}^{CHCl_3}$ 5.77 (br) μ, λ_{max}^{EtOH} (ε) 290 (40), 430 (12) mμ, which failed to enolize.[6] Ozonolysis of II followed by treatment with basic

IV

VII, R = CH₃
VIII, R = H
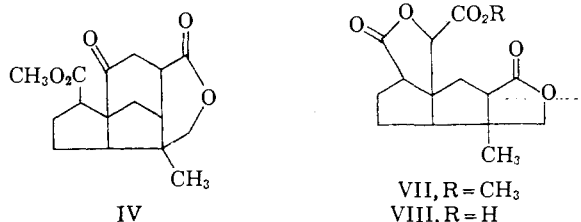
hydrogen peroxide and with diazomethane gave an ester, VII, m.p. 158–159°, $\lambda_{max}^{CHCl_3}$ 5.66 (s), 5.80 μ.[7] The relationship of the groups attached to the six-membered ring was corroborated by the formation of *m*-hydroxybenzoic acid on fusion of II with alkali. Oxidation of II with 6 equiv. of chromic acid gave an acid IX, which was converted by methyl iodide and potassium carbonate to the triester X, m.p. 99.5–100°, $\lambda_{max}^{CHCl_3}$ 5.78, 5.93, 6.10 μ, λ_{max}^{EtOH} 240 mμ (ε 8,700). The acid IX was

(3) C. Harries and W. Nagel, *Ber.*, 55, 3833 (1922); W. Nagel and W. Mertens, *ibid.*, 70, 2173 (1937); 72, 985 (1939).

(4) P. M. Kirk, P. E. Spoerri and W. H. Gardner, THIS JOURNAL, 63, 1243 (1941).

(5) Satisfactory elementary analyses have been obtained for each new compound characterized by m.p. and infrared spectrum.

(6) Further, the n.m.r. spectrum of the diacetate, VI, m.p. 126–127.5°, $\lambda_{max}^{CHCl_3}$ 5.76 (br), 6.09 μ, λ_{max}^{EtOH} 223 mμ (ε 8500), shows the band attributable to the >CHOAc proton as a doublet (τ = 4.29, $J \sim 3$ c./s.).

(7) This compound has been obtained previously *via* oxidation of I to VIII with potassium permanganate.[8]