desosamine, dihydroerythronolide B (I) $C_{21}H_{40}O_7$, m.p. 182°, [Found: C, 62.69; H, 10.01; C-CH_3, 19.92; mol. wt., 410.3 (ebull. in acetone); $\alpha^{25}D$ +6° (*c*, 1 in methanol)] which consumed one mole of sodium metaperiodate, demonstrating that removal of desosamine ($C_8H_{17}NO_3$) liberates an α-glycol system.

Oxidation of I with periodate yielded the syrupy aldehydo-ester-methyl ketone (III) (increased carbonyl absorption, positive iodoform test), which was oxidized with peroxytrifluoroacetic acid[12] to the semi-solid ester-acetate (IV) (no carbonyl absorption in the ultraviolet). Saponification of (IV) at *p*H 12 gave the known *meso*-α,α'-dimethyl-β-hydroxyglutaric acid[13] (V) and the crystalline C_{12}-tetrol (VI), $C_{12}H_{26}O_4$, m.p. 146–148° [Found: C, 61.64; H, 11.38; C-CH_3, 21.62; mol. wt., 231 (ebull. in acetone); $\alpha^{25}D$ −2° (*c* 1 in methanol)] which was stable toward periodate and did not give an iodoform test.

Isolation of the C_7-dicarboxylic acid (V) and C_{12}-tetrol, and demonstration of a methyl ketone function in III,[14] satisfactorily account for the 21 carbon atoms of I.

On the basis of the above data and in view of the common biogenesis of erythromycin and erythromycin B, we propose structure I[15] for dihydroerythronolide B, which differs from the structure established for dihydroerythronolide[1] merely in the absence of a hydroxyl substituent at the carbon atom (C-12) adjacent to the lactone termination point. The lack of this hydroxyl function in erythromycin B apparently precludes the irreversible, acid-catalyzed formation of a spiro-ketal which, in erythromycin, leads to inactivation of the molecule.

[12] W. D. Emmons and G. B. Lucas, THIS JOURNAL, **77**, 2287 (1955).

[13] Isolation of the same *meso*- acid (V) from dihydroerythronolide (see reference footnote 1) is evidence of an extensive structural similarity between the aglycones of the cognate antibiotics, erythromycin and erythromycin B. Obviously, desosamine is substituted at the C-5,6 α-glycol system of I; a tentative assignment of substitution at C-5 as shown in II has been made on the basis of analogous substitution of desosamine in erythromycin.

[14] The experimental conditions employed made isolation of acetic acid formed by oxidation of III impractical.

[15] The configurations of the asymmetric carbon atoms in I (and VI), with the exception of carbons C-2 and C-4 have been drawn on arbitrary basis. Carbons C-2 and C-4 in I correspond to the two methyl-substituted carbons in the *meso*-acid (V) and must, therefore, have identical configuration.

LILLY RESEARCH LABORATORIES
INDIANAPOLIS 6, INDIANA

KOERT GERZON
ROSEMARIE MONAHAN
OLLIDENE WEAVER
MAX V. SIGAL, JR.
PAUL F. WILEY

RECEIVED OCTOBER 15, 1956

THE REACTION BETWEEN TRIETHYL PHOSPHITE AND ALKYL AND ARYL-SULFONYL CHLORIDES

Sir:

We wish to give a preliminary report on a novel reaction of general character, which was observed when triethyl phosphite was treated with alkyl- or arylsulfonyl chlorides. This reaction, which can be represented by the general equation

$$3(C_2H_5O)_3P + RSO_2Cl \longrightarrow \underset{(I)}{(C_2H_5O)_2P(O)SR} + C_2H_5Cl + \underset{(II)}{2(C_2H_5O)_3PO} \quad (1)$$

gives instead of the expected sulfonylphosphonate (III) the corresponding O,O-diethyl S-alkyl (or aryl) phosphate (I) in good yields with the simultaneous formation of two mole equivalents of triethyl phosphate (II). Even in the presence of a large excess of sulfonyl chloride over triethyl phosphite, it was not possible to obtain III; the phosphorus-containing products obtained under a wide variety of conditions were always I and II.

The statement by Kosolapoff[1] that sulfonylphosphonates are apparently unstable is confirmed by our observations, although the references cited in the chapter on the reactions of trialkyl phosphites refer actually to the reactions of dialkyl sodium phosphites with sulfonyl halides.

The I formed from the sulfonyl chlorides might suggest that the first step of the reaction is a reduction to the corresponding sulfenyl chloride which then in turn reacts with triethyl phosphite to yield I according to the general reaction reported by Morrison.[2] This possible reaction route is substantiated somewhat by the fact that aromatic sulfonyl fluorides, which are not affected by reducing agents,[3] were found to be unreactive toward triethyl phosphite. This, however, does not rule out the possibility that the reaction proceeds by a Michaelis–Arbuzov type condensation forming first the unstable intermediate III which is then reduced by triethyl phosphite to I.

The general character of the reaction represented by equation (1) could be demonstrated by the formation of the corresponding thiol phosphates I in good yields from triethyl phosphite and a series of sulfonyl chlorides, RSO_2Cl, where R is CH_3, C_2H_5, Bu, C_6H_5, *o*-MeC_6H_4, *p*-MeC_6H_4, *p*-FC_6H_4, *p*-BrC_6H_4, *m*-$HO_2CC_6H_4$, and 2-$C_{10}H_7$. Substitution of the phenyl ring of benzenesulfonyl chloride in various positions by electron-donating or withdrawing groups was found not to change the generality of the reaction. A detailed study of the effect of different R groups on the yields of I and of the mechanism of the reaction is under way. The results of a typical example each for the reaction of an alkyl- and arylsulfonyl chloride with triethyl phosphite are described briefly in the following paragraph.

The reaction between triethyl phosphite and *n*-butylsulfonyl chloride gave an 87.5% yield of O,O-diethyl S-butyl phosphate, b.p. 94–5° (0.5–0.7 mm.), $n^{25}D$ 1.4550 (calcd. for $C_8H_{19}O_3PS$: C, 42.29; H, 8.43; P, 13.67; S, 14.17: Found: C, 42.6; H, 8.7; P, 14.04; S, 14.23); and 82.5% of slightly impure triethyl phosphate, b.p. 40–42° (0.25–0.30 mm.), $n^{25}D$ 1.4061 (lit.[4]) b.p. 90° (10 mm.), $n^{25}D$ 1.4039 (identified further by comparison of its infrared spectrum with that of an authentic sample); 60% of the theoretical amount of ethyl chloride was collected in an attached cold trap. The reaction between triethyl phosphite and *p*-bromobenzenesulfonyl chloride yielded 87% of

[1] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 197.

[2] D. C. Morrison, THIS JOURNAL, **77**, 181 (1955).

[3] J. H. Simons, "Fluorine Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 179.

[4] D. P. Evans, W. C. Davies and W. J. Jones, *J. Chem. Soc.*, 1310 (1930).

O,O-diethyl S-(*p*-bromophenyl)-phosphate, b.p. 115–117° (40 μ), $n^{25}\text{D}$ 1.5445 (calcd. for $C_{10}H_{14}O_3PSBr$: 36.93; H, 4.34; S, 9.62; Br, 24.39); 96% of triethyl phosphate, b.p. 33° (0.15 mm.), $n^{25}\text{D}$ 1.4036; and 81% of ethyl chloride.

CHEMICAL RESEARCH DIVISION
DIRECTORATE OF RESEARCH FRIEDRICH W. HOFFMANN
CHEMICAL WARFARE LABORATORIES THOMAS R. MOORE
ARMY CHEMICAL CENTER, MD. BENJAMIN KAGAN

RECEIVED OCTOBER 24, 1956

THE DESULFURIZATION OF MERCAPTANS WITH TRIALKYL PHOSPHITES

Sir:

The attempted extension of the transesterification of triethyl phosphite with aliphatic alcohols[1] to mercaptans resulted in the formation of triethyl thionophosphate with simultaneous conversion of the alkanethiol to the corresponding alkane according to the equation $(C_2H_5O)_3P + RSH \rightarrow (C_2H_5O)_3PS + RH$. This unusual desulfurization reaction proceeds practically to completion at reflux temperature during several hours, or at a slower rate at room temperature, and is effectively catalyzed by ultraviolet irradiation.

Thus, a mixture of 83 g. (0.5 mole) of triethyl phosphite (previously distilled from sodium) and 73 g. (0.5 mole) of *n*-octyl mercaptan in a Pyrex flask fitted with a 24-in. fractionating column was irradiated with a General Electric 100-watt S-4 bulb at a distance of 5 inches from the flask. After 6.25 hours of irradiation, the mixture was distilled to give 50.3 g. (88%) of octane, b.p. 122.0–124.5°, $n^{25}\text{D}$ 1.3951–1.3959 (reported,[2] b.p. 125.59°, $n^{25}\text{D}$ 1.3953) and 90.9 g. (0.459 mole) of triethyl thionophosphate, b.p. 45° (0.50 mm.), $n^{20}\text{D}$ 1.4461 (reported,[3] b.p. 105–106° (20 mm.), $n^{20}\text{D}$ 1.4480, calcd. $n^{25}\text{D}$ 1.4460).

Likewise, 83 g. (0.5 mole) of triethyl phosphite and 62 g. (0.5 mole) of benzyl mercaptan were treated in an identical manner to give 43.1 g. (93.6%) of crude toluene, b.p. 90–110°, $n^{25}\text{D}$ 1.4945 (reported[4] 110.56°, $n^{20}\text{D}$ 1.4963, calcd. $n^{25}\text{D}$ 1.4942) and 94 g. (95%) of crude triethyl thionophosphate, b.p. 55° (0.9 mm.), $n^{25}\text{D}$ 1.4461–1.4500, contaminated with some benzyl mercaptan, b.p. 194°, $n^{25}\text{D}$ 1.5715.

Preliminary results show that a wide variety of thiols undergoes the reported desulfurization reaction with triethyl and other trialkyl phosphites. The results of a current investigation of the scope and mechanism of the reaction will be reported later.

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(1) F. W. Hoffmann, R. P. Usinger, Jr., and R. J. Ess, THIS JOURNAL, **78**, 5817 (1956).

(2) A. F. Shepard, A. L. Henne and T. Midgley, Jr., *ibid.*, **53**, 1948 (1931).

(3) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 258.

(4) W. T. Richard and J. H. Wallace, Jr., THIS JOURNAL, **54**, 2705 (1932).

CHEMICAL RESEARCH DIVISION FRIEDRICH W. HOFFMANN
DIRECTORATE OF RESEARCH RICHARD J. ESS
CHEMICAL WARFARE LABORATORIES THOMAS C. SIMMONS
ARMY CHEMICAL CENTER, MD. ROBERT S. HANZEL

RECEIVED NOVEMBER 12, 1956

LABELING OF BENZENE WITH A CARBON-14 ION BEAM[1]

Sir:

A recent communication[2] described the production of labeled organic material with accelerated tritium ions, and the suggestion was made that C^{14} ions might be used for the same purpose. The labeling of organic compounds by C^{14} atoms derived from the $N^{14}(n,p)C^{14}$ reaction has been reported by several workers.[3] However, organic compounds thus labeled (using a nuclear reactor) are subjected to high neutron and gamma ray fluxes, and, in addition, the energy of the C^{14} atom (about 45,000 e.v.) is fixed. Both of these factors cause radiation decomposition to become a serious problem. During the past several months we have been observing the effects produced on irradiating solid benzene with a C^{14} ion beam in a mass spectrometer. Work in this direction has already been reported by Croatto and Giacomello.[4] Since there is great theoretical and practical interest in this type of experiment, we wish to present the results we have obtained in determining the efficiency of a C^{14} ion beam in labeling solid benzene. Benzene was chosen for this work because it is resistant to radiation decomposition and because its purification may be carried out with high efficiency by means of vapor-phase chromatography.

The carbon-14 ion beam was obtained using a 60°-sector, 15-cm. radius mass spectrometer. Labeled carbon dioxide (23% C^{14}) was introduced into the ion source and the singly charged, mass-14 beam thus produced (energy = 2 kv.) amounted to between 10^{-9} and 10^{-10} amp. During the irradiations, benzene vapor was directed slowly and continuously onto the surface of a cold trap at the target end of the spectrometer. This trap was maintained at $-155 \pm 5°$; a lower temperature would have led to condensation of carbon dioxide from the ion source.

The irradiated benzene (about 500 mg.) was purified by repeated passages through vapor-phase chromatographic columns[5] (elution-partition type); two different substrate liquids, silicone and Carbowax, were used.[6] Since labeled toluene is also a possible product in these irradiations,[7] toluene was added to the benzene after an irradiation and the toluene fraction was purified on the chromatographic columns along with the benzene. The specific radioactivity of the benzene and toluene fractions was determined by liquid-scintillation counting.

Two passages through Carbowax columns are

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(1) The work described in this paper was sponsored by the U. S. Atomic Energy Commission.

(2) R. Wolfgang, T. Pratt and F. S. Rowland, THIS JOURNAL, **78**, 5132 (1956).

(3) *E.g.*, P. E. Yankwich, *et al.*, *J. Chem. Phys.*, **14**, 131 (1946); G. Giacomello, *Ricerca sci.*, **21**, 1211 (1951); A. P. Wolf and R. C. Anderson, THIS JOURNAL, **77**, 1608 (1955); A. G. Schrodt and W. F. Libby, *ibid.*, **78**, 1267 (1956).

(4) Abstracts of the Naples, 1954, Meeting of the Italian Society for Scientific Progress (S.I.P.S.). See also *Ricerca sci.*, **26**, 529 (1956).

(5) We wish to thank Drs. K. P. Dimick and J. Corse, Department of Agriculture, Western Utilization Research Branch, Albany, California, for the use of their vapor-phase chromatography apparatus.

(6) K. P. Dimick and J. Corse, *J. Food Tech.*, **10**, 360 (1956).

(7) A. G. Schrodt and W. F. Libby, THIS JOURNAL, **78**, 1267 (1956).