paper impregnated with 0.1 $M$ pH 6 potassium phosphate buffer showed only one round zone of activity against both *Staphylococcus aureus* and *Escherichia coli* plates at $R_f$ 0.65–0.68.

The pure salt in tube serial dilution inhibited *Bacillus subtilis* ATCC 6633 and *Staphylococcus aureus* ATCC 6538P at 0.122 $\gamma$/ml. When it was tested against various microorganisms by agar serial dilution, the results shown in Table I were obtained.

B.—The penicillin could also be made in 38% yield by shaking equivalent amounts of N-chloroformyl-N-phenylglycine and sodium 6-aminopenicillinate in ethyl acetate for 5 min.

C.—3-Phenyl-2,5-oxazolidinedione (3.54 g., 0.02 mole) in 100 ml. of dioxane was added to a stirred solution of sodium 6-aminopenicillinate (2.38 g., 0.01 mole) in 300 ml. of water at 5°. After 2 hr. at 5° the reaction was stopped, and the crude penicillin was isolated as in A. The yield was 97%, $R_f$ 0.68.

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## The Adduct of Triphenylphosphine and Maleic Anhydride

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The reports of Chopard and Hudson[1] prompt us to report work which confirms their results. The reaction of triphenylphosphine with maleic anhydride in an inert solvent gave an adduct which, on recrystallization from benzene, agreed in melting point and analysis with earlier results.[2] Since the infrared spectrum did not conform to that expected for the proposed[2] structure I, other possibilities were considered (II–IV). Aksnes has proposed[3] III to be the correct formulation based on infrared evidence alone.



I      II      III      IV
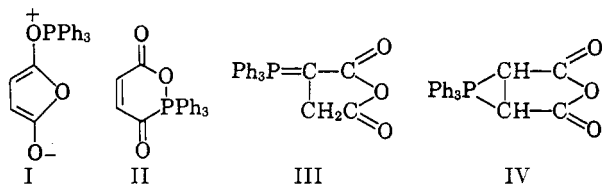
The adduct showed the following properties. Titration of a dioxane solution with aqueous base indicated a monobasic acid.[4] Decomposition at the melting point resulted in formation of triphenylphosphine. The $P^{31}$ n.m.r. spectrum showed a peak at $-13$ p.p.m. relative to phosphoric acid. Compounds containing five groups attached to a phosphorus atom have been reported[5] to show a large positive shift. The proton magnetic resonance showed two nonvinylic protons[6] and 15 aromatic hydrogen atoms.

(1) (a) R. F. Hudson and P. A. Chopard, *Helv. Chim. Acta*, **46**, 2178 (1963); (b) P. A. Chopard and R. F. Hudson, *Z. Naturforsch.*, **18b**, 509 (1963).
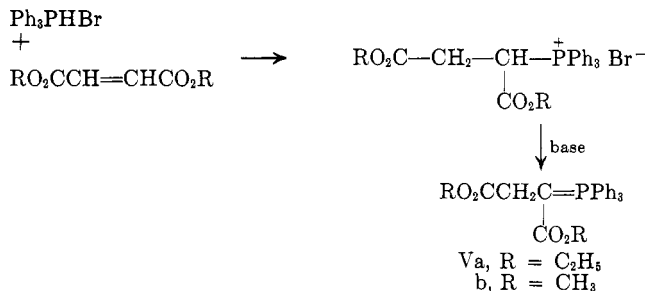
(2) A. Schonberg and A. F. A. Ismail, *J. Chem. Soc.*, 1374 (1940).

(3) G. Aksnes, *Acta Chem. Scand.*, **15**, 692 (1961).

(4) On the basis of III, this can be rationalized by assuming that the half-acid sodium salt $(Ph_3P=C-CH_2-CO_2H\ Na^+$ or $Ph_3P=C(CO_2H)-$
$\quad\quad\quad\quad\quad |$
$\quad\quad\quad\quad\quad CO_2^-$
$CH_2-CO_2^-Na^+)$ can tautomerize to a stable zwitterion $(Ph_3P^+-CH-(CO_2^-)-CH_2-CO_2^-Na^+)$ which may exist as either an open chain as shown or as a cyclic lactone-type structure containing phosphorus in the ring.

(5) R. A. Y. Jones and A. R. Katritzky, *Angew. Chem., Intern. Ed.*, **1**, 32 (1962).

(6) The nonaromatic protons appear as a single peak. Closer investigation disclosed that a 0.8-c.p.s. coupling was present. This is in essential agreement with the report of Hudson and Chopard.[1a]



$$Ph_3PHBr + RO_2CCH=CHCO_2R \longrightarrow RO_2C-CH_2-CH-\overset{+}{P}Ph_3\ Br^-$$
$$|$$
$$CO_2R$$
$$\downarrow base$$
$$RO_2CCH_2C=PPh_3$$
$$|$$
$$CO_2R$$

Va, R = $C_2H_5$
b, R = $CH_3$

Since III was the only tenable structure remaining, the adduct was related to a known substance by the following route. The reaction of triphenylphosphine hydrobromide with diethyl fumarate followed by treatment with base has been reported[7] to give Va. When dimethyl fumarate was used, Vb was obtained in 69% yield. Treatment of the adduct III with methanol[8] followed by diazomethane also gave Vb in 82.5% yield. Furthermore, Vb has been previously prepared by an alternate route.[9,10]

We have also found that chloromaleic anhydride reacts with triphenylphosphine to give an adduct having the same characteristic infrared spectrum as the maleic anhydride adduct. Citraconic anhydride did not react in this fashion but gave, instead, an unidentified, red solid which contained only one carbonyl band in the infrared spectrum.

### Experimental

**Triphenylphosphine–Maleic Anhydride Adduct.**—Equimolar amounts of triphenylphosphine and maleic anhydride solutions in benzene were mixed with stirring. The precipitated product was washed and dried to give a crude, orange, amorphous-looking powder in 92.8% yield. An analytical sample was obtained from benzene, m.p. 162.5–163.5° dec., lit.[2] m.p. 160° dec.

*Anal.* Calcd. for $C_{22}H_{17}O_3P$: C, 73.33; H, 4.75; P, 8.60; equiv. wt., 360 (monobasic), 180 (dibasic). Found: C, 73.58; H, 4.78; P, 8.39; equiv. wt., 366.

The infrared spectrum (mull in mineral oil) showed two strong carbonyl bands at 1682 and 1787 cm.$^{-1}$. In KBr these bands are reported[3] to appear at 1702 and 1805 cm.$^{-1}$.

**Triphenylphosphinecarbomethoxymethylcarbomethoxymethylene (Vb).**—Methanol (2 ml.) was added to 208 mg. of adduct III and the solution refluxed 15 min. After cooling, an ether solution of diazomethane was added until no further signs of reaction occurred and the mixture had a definite yellow color. The solvent was then removed under reduced pressure, and the resulting oil was triturated in ether to form a tan solid. One recrystallization from chloroform-$n$-hexane gave 193 mg. of product, m.p. 156–158° (lit.[9] m.p. 157–158°) alone and 163–165° when mixed with an authentic sample prepared as follows. To 721 mg. of dimethyl fumarate in 10 ml. of acetonitrile was added 1.716 g. of triphenylphosphine hydrobromide (prepared by bubbling HBr into an ether solution of triphenylphosphine), and the mixture refluxed 30 min. The mixture was diluted with water and extracted with ether; the aqueous layer was neutral-

(7) H. Hoffmann, *Chem. Ber.*, **94**, 1331 (1961).

(8) The resulting half-ester was not purified, but the crude material had the reported[1a] infrared spectrum. The proton n.m.r. spectrum of this crude material did not show the expected CH–CH_2 splitting required for the structure proposed by Hudson and Chopard.[1] Instead, a doublet ($J$ = 15 c.p.s.) arising from the CH_2 group and split by PH coupling was observed at 2.86 p.p.m. (TMS = 0). The methyl group appeared at 3.3 p.p.m. as a sharp singlet. The H atom presumed to be on oxygen did not give a discernible peak.

(9) H. J. Bestmann and H. Schulz, *Chem. Ber.*, **95**, 2921 (1962).

(10) The proton n.m.r. spectrum of Vb showed a doublet ($J$ = 17 c.p.s.) at 2.93 (2H), a sharp peak at 3.43 (3H), a broad band at 3.28 p.p.m. (3H), and the expected aromatic band (15H). We have no explanation for the anomalous behavior of one of the methyl groups of this diester nor for the absence of PH splitting in the anhydride III despite the apparent presence of such splitting in the mono- and diester. That the observed splitting in Vb ($J$ = 17 c.p.s.) is due to PH coupling and not nonequivalent H's was confirmed by the fact that at 100 Mc. the coupling was unchanged ($J$ = 17.3 c.p.s.).

ized with 2 N NaOH. The resulting solid was filtered, washed, and dried to give 1.405 g., 69.2%, of crude product. An analytical sample was obtained from chloroform–n-hexane, m.p. 165.5–167°

Anal. Calcd. for $C_{24}H_{23}O_4P$: C, 70.93; H, 5.70; P, 7.62; mol. wt., 406. Found: C, 70.95; H, 5.91; P, 7.69; mol. wt., 379.

The infrared spectra of the esters prepared by the two methods were superimposable and showed two strong carbonyl bands at 1725 and 1610 cm.$^{-1}$.

**Reaction of Other Anhydrides with Triphenylphosphine.**— Ethereal solutions of equimolar amounts of chloromaleic anhydride and triphenylphosphine were mixed to give a purple precipitate in 94% yield. The infrared spectrum of the crude product showed absorption bands at 1775 and 1705 cm.$^{-1}$ (in mineral oil). Efforts to obtain pure material by recrystallization have been unsuccessful.

When ether solutions of citraconic anhydride (1.12 g.) and triphenylphosphine (261 g.) were mixed, no visible reaction occurred even after refluxing and then allowing the mixture to stand 4 hr. The solvent was removed under vacuum and the tan crystalline mass was allowed to stand overnight. The resulting mixture was deep red and, after washing with ether, gave 1.53 g. of a red, crystalline solid, m.p. 100–103.5° dec. The infrared spectrum (mineral oil) showed a strong band at 1770 cm.$^{-1}$. Unreacted triphenylphosphine (2.05 g.) was recovered from the ether washings.

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# The Structure of Two New Dibromobenzofurazan Oxides from the Dehydrobromination of Tetrabromotetrahydrobenzofurazan Oxide

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During an investigation of substituted benzofurazan oxides for fungicidal activity, it was found that treatment of tetrabromotetrahydrobenzofurazan oxide (I) with several nucleophiles yielded two dibromobenzofurazan oxides which had not been described previously.



a, $X_1 = Br$, $X_2 = X_3 = H$
b, $X_2 = Br$, $X_1 = X_3 = H$
c, $X_3 = Br$, $X_1 = X_2 = H$
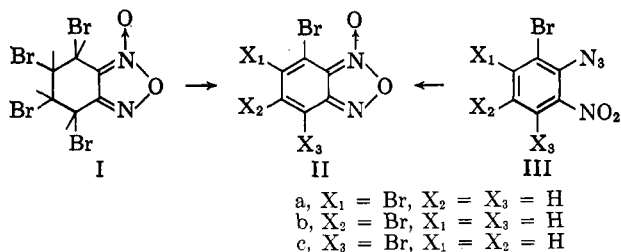
Treatment of I with aqueous alkali has been shown to produce a dibromobenzofurazan oxide melting at 132°.[2a] The structure was originally postulated as IIb but was later established as IIc by reduction to the known 3,6-dibromo-o-phenylenediamine.[2b]

In the present study, when I, m.p. 169–170°, was treated with pyridine or potassium acetate in glacial acetic acid, a mixture of two new dibromobenzofurazan oxides was formed. One of these had m.p. 148–149° and the other had m.p. 92.5–93°.

The four possible dibromobenzofurazan oxides were synthesized and compared with these two products. The synthesis of IIa, IIb, and IIc was accomplished by ring closure in refluxing toluene of the corresponding azidodibromonitrobenzenes (IIIa, IIIb, and IIIc) which were prepared by diazotization[3] of the corresponding dibromo-o-nitroanilines and treatment of the diazonium salts with sodium azide. 5,6-Dibromobenzofurazan oxide was prepared from 4,5-dibromo-2-nitroaniline[4] by oxidation with alkaline hypochlorite.[5]

The products melting at 148–149° and 92.5–93° were found to be identical with synthetic 4,5- and 4,6-dibromobenzofurazan oxide (IIa and IIb), respectively, by mixture melting point and comparison of their infrared spectra. The four dibromobenzofurazan oxides were converted to the corresponding furazans by reduction with hydroxylamine in alkaline solution followed by steam distillation.[6]

The effect of the nucleophile and the solvent on the isomer distribution produced in the dehydrobromination of I is currently under investigation.

## Experimental[7]

**Preparation of Compounds. Dibromo-o-nitroanilines.**—5,6-Dibromo-2-nitroaniline was prepared in a four-step reaction sequence: o-bromoaniline → 2-bromo-6-nitroaniline[8,9] → 2,3-dibromonitrobenzene[3,10] → 2,3-dibromoaniline[11] → 5,6-dibromo-2-nitroaniline.[12] The last step in the reaction sequence was conducted as follows. 2,3-Dibromoaniline was acetylated to give 2,3-dibromoacetanilide, and 7.0 g. (0.024 mole) of the latter was slowly added with vigorous agitation to 15 ml. of fuming nitric acid (sp. gr. 1.51) at −5°. After 1 hr. at 0° the orange solution was added dropwise to an ice–water mixture to produce a yellow precipitate, which was filtered, washed with water, and recrystallized from 95° ethanol to give 3.27 g. (40%) of 5,6-dibromo-2-nitroacetanilide[12] as fine white needles, m.p. 235–237° dec. A suspension of 4.69 g. (0.014 mole) of the latter in a mixture of 50 ml. of 95% ethanol plus 12 ml. of concentrated hydrochloric acid was refluxed for 48 hr. The suspension was diluted with hot 95% ethanol (ca. 30 ml.) to produce a solution which on cooling deposited 3.88 g. (94%) of 5,6-dibromo-2-nitroaniline as yellow needles, m.p. 150.5–151°, lit.[12] m.p. 149°.

4,5-Dibromo-2-nitroaniline was prepared in 75% yield via the ethyl nitrate nitration of 3,4-dibromoacetanilide to 4,5-dibromo-2-nitroacetanilide,[4] followed by acid hydrolysis as above, forming orange needles, m.p. 203.5–204.5°, lit.[4] m.p. 204–205°.

4,6-Dibromo-2-nitroaniline was prepared in 84% yield by the bromination of o-nitroaniline in glacial acetic acid, forming orange needles, m.p. 127–128° (from 95% ethanol), lit.[13] m.p. 127–128°.

3,6-Dibromo-2-nitroaniline was prepared by Austin's procedure,[14] heating 2,3-dinitro-1,4-dibromobenzene in a sealed tube with ammonia for 3 hr. at 100° and, much more conveniently, by passing ammonia through a suspension of the compound in ethanol. Thus, anhydrous ammonia was bubbled through a suspension of 2.0 g. (6.1 mmoles) of 2,3-dinitro-1,4-dibromoben-

(1) Deceased Aug. 12, 1964.
(2) (a) D. L. Hammick, W. A. M. Edwards, and E. R. Steiner, J. Chem. Soc., 3308 (1931); (b) J. H. Boyer, U. Toggweiler, and G. A. Stoner, J. Am. Chem. Soc., 79, 1748 (1957).

(3) H. H. Hodgson and J. Walker, J. Chem. Soc., 1620 (1933).
(4) F. H. Case, J. Org. Chem., 16, 941 (1951).
(5) A. G. Green and F. M. Rowe, J. Chem. Soc., 101, 2452 (1912).
(6) T. Zincke and P. Schwarz, Ann., 307, 28 (1899).
(7) Melting points are uncorrected and were determined on a Thomas–Hoover melting point apparatus, spectra were taken with a Perkin-Elmer Model 137-B infrared spectrophotometer, and analyses were by Elek Microanalytical Laboratories, Torrance, Calif.
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(9) H. Franzen and E. Engel, J. prakt. Chem., 102, 156 (1921).
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(11) G. Körner and A. Contardi, Atti accad. naz. Lincei Mem. Classe sci. fis. mat. e nat., [5] 15, 526 (1906).
(12) G. Körner and A. Contardi, ibid., [5] 15, 580 (1906).
(13) C. L. Jackson and F. W. Russe, Am. Chem. J., 35, 148 (1906).
(14) P. T. Austin, Ber., 9, 621 (1876).