of the corresponding sulfide with *m*-chloroperbenzoic acid according to the usual procedure. Infrared spectra were measured in Nujol mulls with a Perkin-Elmer Model 337 spectrophotometer. The spectrum of thiazine **2a** showed major bands at 3258, 1630, 1516, 1242 (vs), 1104 (vs), and 709 cm$^{-1}$. The spectrum of thiazine **2b** had major bands at 3270, 3230, 1635, 1523, 1230 (vs), 1156, 1088 (vs), 761, 726, and 698 cm$^{-1}$.

**Registry No.**—**2a**, 14953-99-2; **2b**, 14954-06-4; **3a**, 12310-21-3; **3b**, 12310-20-2.

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## Reaction of Diethyl Bromomalonate with Sodium Diethyl Phosphite[1]

K. H. Takemura and Dean J. Tuma

*Department of Chemistry, The Creighton University, Omaha, Nebraska 68131*

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The reaction of diethyl bromomalonate (**1**) and sodium diethyl phosphite (**2**) in ether has been reported to yield tetraethyl 1,1,2,2-ethanetetracarboxylate (**3**).[2] As part of a study of the reactions of **1** with nucleophilic agents, we have reinvestigated this reaction.

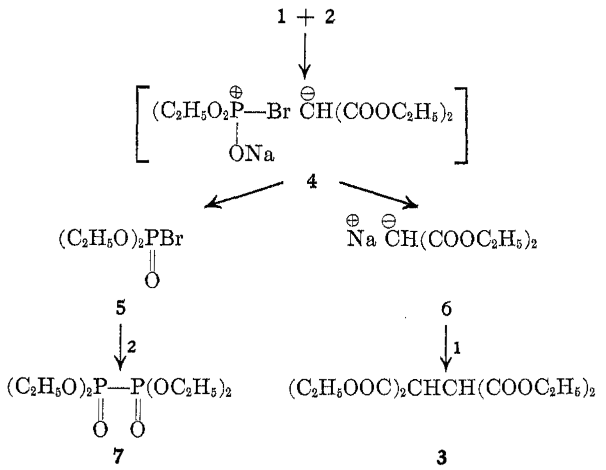
$$\underset{\mathbf{1}}{BrCH(COOC_2H_5)_2} + \underset{\mathbf{2}}{(C_2H_5O)_2PONa} \longrightarrow \underset{\mathbf{3}}{(C_2H_5OOC)_2CHCH(COOC_2H_5)_2}$$

The most apparent mode of formation of the tetraester (**3**) is a nucleophilic substitution reaction between **1** and malonate anion. This is supported by our observations which we wish to report here, together with additional features of the reaction. The sequence of reactions in Scheme I describes the transformation of **1** into **3**.

The first step is suggested by those reports on the reactions between tervalent phosphorus and bromo compounds in which attack on halogen is postulated.[3] Initial displacement on bromine has been proposed in the debromination of $\alpha$-bromo ketones with triphenylphosphine in protic media.[4]

The addition of ethanol to the reaction of **1** with **2** in ether gave a smaller yield of tetraester **3**. The major products of the reaction were diethyl malonate (**8**) and triethyl phosphate (**9**). These were the only products when the reaction was carried out in ethano as solvent; no **3** was observed.[5] The difference in behavior observed in some cases with chlorine derivatives, *e.g.*, diethyl chloromalonate does not react with **2** under these conditions,[2] lends further support for the first step. The difference may be attributed to the greater polarizability of bromine which makes reaction on halogen more favorable.

Scheme I



$$\mathbf{4} + C_2H_5OH \longrightarrow \underset{\mathbf{8}}{CH_2(COOC_2H_5)} + \underset{\mathbf{9}}{(C_2H_5O)_3PO}$$

Additional evidence for the first step was found in reactions performed in the presence of benzyl bromide. In addition to **3**, diethyl benzylmalonate (**10**) was obtained, the latter resulting from the reaction of malonate anion with benzyl halide. Some diethyl benzylphosphonate (**11**) was also formed in these reactions.

$$\underset{\mathbf{10}}{C_6H_5CH_2CH(COOC_2H_5)_2} \qquad \underset{\mathbf{11}}{(C_2H_5O)_2P(O)CH_2C_6H_5}$$

Moreover, when bromo ester **1** was added to a large excess of the phosphite (**2**), followed then by the addition of benzyl bromide, a large amount of **10** was found but none of the tetraester (**3**). Under these conditions it appeared that all of the bromo ester had been converted into the ion pair (**4**), thus preventing the formation of **3**. To exclude the possibility that the benzyl malonate (**10**) had actually arisen from the reaction of **1** with benzyl anion, the reaction of benzyl bromide with phosphite **2** was investigated. The formation of 1,2-diphenylethane would be expected if benzyl anion were generated. This compound, however, was not found. The principal product of the reaction was benzylphosphonate **11**.

In the original preparation of tetraester **3**, equimolar quantities of bromomalonate (**1**) and sodium diethyl phosphite (**2**) were employed.[2] On the basis of our initial view of the reaction, it was anticipated that 0.5 molar equiv of **2** would be sufficient, since it was necessary only for half of the bromo ester to be converted into malonate anion. Experiments, however, revealed that optimum yields of **3** were obtained when

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[1] From the M.S. Thesis of D. J. T., 1968.

[2] A. E. Arbuzov and V. S. Abramov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 223 (1946).

[3] (a) B. Miller in "Topics in Phosphorus Chemistry," Vol. 2, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1965, pp 133–199; (b) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, New York, N. Y., 1965, pp 114–116, 141–160.

[4] I. J. Borowitz and R. Virkhaus, *J. Amer. Chem. Soc.*, **85**, 2183 (1963); P. A. Chopard, R. F. Hudson, and G. K. Klopman, *J. Chem. Soc.*, 1379 (1965); I. J. Borowitz, K. C. Kirby, Jr., and R. Virkhaus, *J. Org. Chem.*, **31**, 4031 (1966).

[5] We have attributed the dehalogenation of bromomalonate in ethanol to the action of sodium diethyl phosphite rather than to any diethyl phosphite formed from the sodium salt and alcohol. Debromination with diethyl phosphite occurs more slowly and incompletely (unpublished observations in this laboratory). There is also little reaction between bromomalonate and diethyl phosphite in ether.[1]

equimolar amounts of the reactants were used (see Table I). The apparent irregularity can be accounted for in the following manner. The reaction of phosphite **2** with the bromo ester yields a bromophosphorus species, probably bromophosphate **5** (Scheme I), as well as malonate anion. This reactive bromophosphate is presumed to be responsible for the triethyl phosphate produced in those reactions carried out in the presence of ethanol (see above). In the absence of other nucleophilic species, **5** rapidly combines with phosphite **2** to yield tetraethyl hypophosphate (**7**) and/or other phosphorus derivatives.[6,7] It appears then that one-half of the phosphite **2** is not available for reaction with bromomalonate. In essence, 2 mol of **2** are needed to generate 1 mol of malonate anion. Larger amounts of **2** were found to be undesirable for the formation of tetraester **3**. These conditions lead to higher concentrations of malonate anion but a concomitant decrease in bromomalonate, resulting in lower yield of **3** and increase in the debromination of the bromo ester.

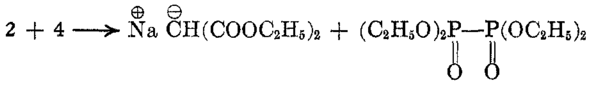
TABLE I

REACTION OF DIETHYL BROMOMALONATE (**1**) AND SODIUM DIETHYL PHOSPHITE (**2**)

| Run[a] | Moles of **2**/ mol of **1** | Yield of tetraester (**3**),[b] % | Other major components in reaction mixture[c] |
|---|---|---|---|
| 1 | 0.5 | 22 | **1** |
| 2 | 1 | 57 | **1** and diethyl malonate |
| 3 | 2 | 45 | Diethyl malonate |
| 4 | 10 | 0 | Diethyl malonate |

[a] All runs were carried out in duplicate. [b] Determined by isolation of product. [c] Vpc analysis.

In Scheme I, the ion pair (**4**) is considered to dissociate into bromophosphate **5** and sodium malonate (**6**), followed by the reaction of **5** with phosphite **2** to yield hypophosphate **7**. An alternative pathway for these tranformations is the direct combination of ion pair **4** with phosphite **2**. The information available



$$2 + 4 \longrightarrow \overset{\oplus}{\mathrm{Na}}\ \overset{\ominus}{\mathrm{C}}\mathrm{H(COOC_2H_5)_2} + \mathrm{(C_2H_5O)_2}\underset{\mathrm{O}}{\underset{\|}{\mathrm{P}}}\mathrm{—}\underset{\mathrm{O}}{\underset{\|}{\mathrm{P}}}\mathrm{(OC_2H_5)_2}$$

**6** **7**

does not permit one to distinguish between the two routes to **6** and **7**.

The conversion of α-bromo ketones by thiol anions

$$\mathrm{RCOCH_2Br} + \mathrm{R'S^{\ominus}} \longrightarrow \mathrm{RCOCH_2CH_2COR} + \mathrm{R'SSR'}$$

to 1,4 diketones has been reported.[8] It was, therefore, anticipated that the conversion of bromomalonate (**1**) to the tetraester **3** could be effected with sodium thiophenoxide. The reaction of **1** with thiophenoxide ion in ether gave **3** and diphenyl disulfide. In ethanol solvent, the principal products were diethyl malonate and the disulfide.

## Experimental Section

All melting points and boiling points are uncorrected. Reagent grade diethyl phosphite and diethyl bromomalonate were purified by distillation, bp 83-84° (17 mm) and 69-70° (0.5 mm), respectively. Sodium diethyl phosphite was prepared in ether for each experiment from diethyl phosphite and metallic sodium. Diethyl benzylphosphonate was prepared according to published procedures:[9] bp 156-158° (13 mm); $n^{25}\mathrm{D}$ 1.4957 [lit. bp 155° (14 mm),[9a] bp 153-154° (11 mm), $n^{20}\mathrm{D}$ 1.4965[9b]]. All other chemicals were of reagent quality and were used without further purification. Vpc analyses were carried out on a 6 ft × 0.25 in. column of 20% SE-30 on Chromosorb W at 150-200°.

**Reaction of Diethyl Bromomalonate (1) and Sodium Diethyl Phosphite (2). A. In Ether.**—In a typical run, 4.0 g (0.017 mol) of **1** in 9 ml of ether was added dropwise, with stirring at room temperature, to 0.017 mol of **2** in 50 ml of ether. A vigorous reaction occurred with rapid precipitation of sodium bromide. The reaction mixture was then refluxed for 45 min, and diluted with water. The ether layer was separated, washed with water, and dried ($\mathrm{Na_2SO_4}$). Evaporation of the ether left a viscous oil which crystallized from ethanol-water to give white crystals: yield 1.52 g (57%); mp 70-73°. Recrystallization from ethanol-water afforded tetraethyl 1,1,2,2-ethanetetracarboxylate (**3**) as white needles, mp 76° (lit.[2] mp 76°).

*Anal.* Calculated for $\mathrm{C_{14}H_{22}O_8}$: C, 52.83; H, 6.97. Found: C, 52.83; H, 7.19.

Vpc analysis of the mother liquor showed that the major components were approximately equimolar amounts of unchanged **1** and diethyl malonate.

**B. In the Presence of Ethanol.**—The reaction described in A was repeated except that 1.5 ml (0.026 mol) of ethanol was added with the bromo ester. Vpc analysis of the reaction mixture showed diethyl malonate (**8**) and triethyl phosphate (**9**) as the major organic products. The tetraester (**3**) was isolated in 12% yield, mp 70-71°. With 0.17 mol of ethanol only a trace of **3** was found. In ethanol as solvent **3** was not observed. The principal products were **8** and **9**.

**C. In the Presence of Benzyl Bromide. 1.**—The reaction in A was repeated with modification. In one experiment, 5.8 g (0.034 mol) of benzyl bromide was added with the bromomalonate (**1**). Analysis of the oily product by vpc indicated the presence of ester **3**, diethyl benzylmalonate (**10**), and diethyl benzylphosphonate (**11**). The molar ratio of **10** to **3** was approximately 0.1. Repetition of the reaction with 0.059, 0.10, and 0.20 mol of benzyl bromide gave molar ratios of **10**:**3** of 0.3, 1, and 6, respectively. Compound **11** was also formed in these reactions.

**2.**—The reaction with 0.10 mol of benzyl bromide was repeated with increased concentration (0.51 mol) of phosphite **2**. The molar ratio of **10**:**3** formed in the reaction was 3.

**3.**—To 0.017 mol of **2** in 50 ml of ether was added 0.80 g (0.0034 mol) of **1**. The resultant mixture was refluxed for 45 min followed by the addition of 4.1 g (0.024 mol) of benzyl bromide. The mixture was then refluxed for 1.5 hr, and processed as described above. Vpc analysis indicated that the major product was benzylmalonate (**10**). Compound **11** together with a trace of malonate ester **8** was also found, but no tetraester **3**.

**Reaction of Benzyl Bromide and 2.**—To a suspension of 0.017 mol of **2** in 50 ml of ether was added dropwise, with stirring, 8.6 g (0.050 mol) of benzyl bromide. The mixture was then refluxed for 45 min and diluted with water. The ether layer was separated, washed with water, and dried ($\mathrm{Na_2SO_4}$). Evaporation of the ether yielded an oil which was analyzed by vpc. The major product of the reaction was the benzylphosphonate (**11**). 1,2-Diphenylethane was not detected.

**Reaction of Diethyl Bromomalonate (1) and Sodium Thiophenoxide.**—The sodium salt was prepared by the addition of 0.96 g (0.0085 mol) of thiophenol to 0.20 g (0.0085 g-atom) of sodium in 35 ml of ethanol under dry nitrogen. The solvent was then removed under reduced pressure. The dried salt was suspended in 35 ml of ether, followed by the dropwise addition of 2.0 g (0.0085 mol) of **1** in 6 ml of ether. The mixture was heated under reflux for 1.5 hr, and then washed with water. The ether solution was dried ($\mathrm{Na_2SO_4}$) and concentrated. The oily residue was analyzed by vpc; the major components were tetraester (**3**), diphenyl disulfide, diethyl malonate (**8**), and unchanged **1**. The reaction was repeated in ethanol solvent. The principal products were diphenyl disulfide and **8**.

**Registry No.—1,** 685-87-0; **2,** 2303-76-6.

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[6] Reference 3a, p 165.

[7] G. M. Kosalapoff, "Organophosphorus Compounds," John Wiley & Sons, Inc., New York, N. Y., 1950, p 336.

[8] F. Weygand and H. G. Peine, *Rev. Chim. Acad. Rep. Populaire Roumaine*, **7**, 1379 (1962); *Chem. Abstr.*, **61**, 4028 (1964).

[9] (a) B. C. Saunders, G. J. Stacey, F. Wild, and I. G. E. Wilding, *J. Chem. Soc.*, 699 (1948); (b) N. P. Bogonostseva, *Uch. Zap. Kazansk. Gos. Univ.*, **116**, 71 (1956); *Chem. Abstr.*, **51**, 6581 (1957).