chloride.[11a] The reduction step gave *ca.* 3% yield of *m*-mercaptobenzoic acid, m.p. 146–147° (lit.[11] 146–147°). The thiol, 50 ml. of absolute alcohol, and 2 ml. of concentrated sulfuric acid were left for a week at *ca.* 25°. The crude ester was distilled through a small column to yield *m*-carbethoxythiophenol, b.p. 95–100° (0.1 mm.), n_D^{21} 1.5612 [lit.[11b] b.p. 147–149 (11 mm.)]. Amperometric analysis with silver nitrate indicated a purity of 97.5 ± 0.5%.

In the above thiols, any impurities were probably the disulfides. These would not interfere with the infrared measurements of the S—H frequency. Some errors could be introduced in the λ_{max} and ϵ_{max} values. For example, λ_{max} 238–241 mμ and log ϵ_{max} 4.2 have been reported[12] for diphenyl disulfide as compared to λ_{max} 237 mμ and log ϵ_{max} 3.88, which we have found for thiophenol. The ultraviolet spectra of seven undissociated thiols and their anions were taken on a Beckman DK2 recording spectrophotometer in the range 220–340 mμ. λ_{max} and ϵ_{max} were determined and are summarized in Table I. Matched pairs of quartz cells of 1-cm. path length were used. Absolute alcohol was the solvent. Its impurities could not be detected spectroscopically in a 1-cm. cell when run against the reference water. Typical thiol spectra have been given by others.[3]

To obtain the spectrum of an undissociated thiol, one drop of concentrated hydrochloric acid was added to 100 ml. of both the sample solution and the reference solvent. This was enough to suppress the ionization of the thiophenols since the yellow color of the most acidic thiol, *p*-nitrothiophenol, disappears completely. To obtain the spectrum of a thiolate ion, 1 ml. of 0.1*M* sodium ethoxide was added to 100 ml. of both the sample solution and the reference solvent.

The infrared spectra were taken on a Perkin-Elmer Model 21 spectrophotometer equipped with calcium fluoride optics. Sodium chloride or calcium fluoride cells of *ca.* 0.1 mm. thickness were used. The S—H region was scanned slowly at least three times. The scale on the infrared records was 5 cm.$^{-1}$ per cm. of chart. Spectrograde carbon tetrachloride was the usual solvent. As the S—H stretching frequency of benzenethiol shifted from 2570.5 cm.$^{-1}$ in the neat liquid to 2576.5 cm.$^{-1}$ when it was in dilute carbon tetrachloride solution, spectra for all thiols were taken on dilute solutions. Usually two such solutions of different dilutions were used. An internal standard spectrum of benzenethiol in carbon tetrachloride was repeatedly taken during these measurements. The precision of this standard was *ca.* 1.0 cm.$^{-1}$ while that of the other thiols was 1–2 cm.$^{-1}$

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[11] (a) S. Smiles *et al.*, *J. Chem. Soc.*, **119**, 1792 (1921); **121**, 2022 (1922); (b) P. F. Wiley, *J. Org. Chem.*, **16**, 810 (1951).

[12] L. Bauer and J. Cymerman, *J. Chem. Soc.*, **109** (1950); H. P. Koch, *J. Chem. Soc.*, 394 (1949).

Triphenylcarbethoxymethylphosphonium Chloride Dihydrate

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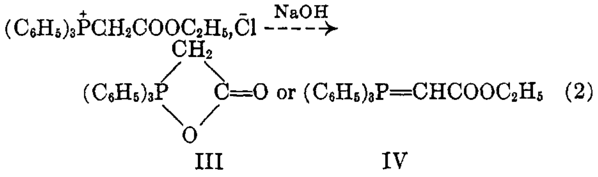
In a paper published in 1894 Michaelis and Gimborn reported[1] that the condensation of ethyl chloroacetate and triphenylphosphine[1] gave triphenylcarbethoxymethylphosphonium chloride (I). In the same paper they also report that treatment of I with sodium hydroxide (2) gave a compound formulated as the betaine (III). Recently Isler and co-workers[2] showed that the bromide analogue of I gives triphenylcarbethoxymethylene phosphorane (IV) on caustic treatment, rather than III. The discrepancy between these two reports led to a reinvestigation of the early work. Some of our results have been anticipated.[3]

$$(C_6H_5)_3P + ClCH_2COOC_2H_5 \dashrightarrow (C_6H_5)_3\overset{+}{P}CH_2COOC_2H_5,\overset{-}{Cl}\cdot nH_2O \quad (1)$$

I. $n = 0$
II. $n = 2$



$$(C_6H_5)_3\overset{+}{P}CH_2COOC_2H_5,\overset{-}{Cl} \xdashrightarrow{NaOH} (C_6H_5)_3P\langle CH_2, O\rangle C{=}O \text{ or } (C_6H_5)_3P{=}CHCOOC_2H_5 \quad (2)$$

III IV

In following Michaelis's directions for the synthesis of the phosphonium chloride (I), difficulties were encountered. Attempts to recrystallize the crude product led invariably to decomposition. This problem was resolved when it became clear from interpretation of the infrared spectra, elementary analysis, and Karl Fisher determination that the product isolated was actually the dihydrate (II). This compound was best synthesized by simply mixing ethyl chloroacetate and a solution of triphenylphosphine in benzene. During standing at room temperature, a crystalline product was formed. The reaction was arbitrarily considered to be complete after a week and the product was filtered and washed with absolute ether. The crude salt was allowed to dry in air—*i.e.* in contact with water vapor—for one week. Under these conditions the dihydrate (II), of analytical purity, was obtained in high yield.

The dihydrate holds its crystalline water tenaciously. It survived recrystallization from methylene chloride–carbon tetrachloride. Long drying of II over phosphorus pentoxide *in vacuo* raised the melting point from 87° to 144°. This higher melting material is probably the anhydrous salt. On exposure to air, its melting point was soon lowered. Since the dihydrate was accessible, stable, and convenient for further work, no attempts were made to characterize the anhydrous salt.

An attempt to dehydrate the dihydrate (II) was made by refluxing with benzene. The products were found to be triphenylmethylphosphonium chloride (VI), carbon dioxide, ethanol and water. Formation of these products is represented by Equation 3. Reaction started as soon as the benzene

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[1] A. Michaelis and H. v. Gimborn, *Ber.*, **27**, 272 (1894)

[2] O. Isler *et al.*, *Helv. Chem. A.*, **XL**, 1242 (1957).

[3] L. C. Smith, thesis, Rutgers University (1960).

$$\begin{aligned}&(C_6H_5)_3\overset{+}{P}CH_2COOC_2H_5,\overset{-}{Cl}\ 2H_2O \longrightarrow\\ &\qquad [(C_6H_5)_3\overset{+}{P}CH_2COOH,\overset{-}{Cl}] \longrightarrow\\ &\qquad \underset{V}{(C_6H_5)_3\overset{+}{P}CH_3,\overset{-}{Cl}} + H_2O + \underset{VI}{C_2H_5OH} + CO_2 \qquad (3)\end{aligned}$$

had reached its boiling point and was complete within three hours.

In contrast to the above behavior, when the hydrolysis of II was carried out at room temperature in dilute hydrochloric acid, the interesting analogue of betaine hydrochloride (V) was obtained. The direct synthesis of V from chloroacetic acid and triphenylphosphine was recently reported by Denney.[4] Comparison of acids from both routes showed them to be identical.

As would be expected from the work on the bromo analogue of I, treatment of II with aqueous sodium hydroxide led to the phosphorane IV in a quantitative yield; a phosphobetaine (III) was not obtained.[3]

The phosphorane IV is soluble in hydrochloric acid and recoverable by immediate neutralization with sodium hydroxide. If a solution of the phosphorane in hydrochloric acid is allowed to evaporate slowly, at room temperature, crystals of V are obtained.[4]

$$\begin{aligned}&\underset{IV}{(C_6H_5)_3P{=}CHCOOC_2H_5} \underset{NaOH}{\overset{HCl}{\rightleftarrows}}\\ &\qquad (C_6H_5)_3\overset{+}{P}CH_2COOC_2H_5,\overset{-}{Cl} \xrightarrow[H_2O]{H^+}\\ &\qquad\qquad \underset{V}{(C_6H_5)_3\overset{+}{P}CH_2COOH,\overset{-}{Cl}} \qquad (4)\end{aligned}$$

EXPERIMENTAL

Materials. Commercial triphenylphosphine was purified by recrystallization from methanol and then hexane; m.p. 80–81°. Ethyl chloroacetate (practical grade) was distilled. Material used boiled at 144–145°. Ethyl bromoacetate —Eastman White Label used as such.

All melting points were taken on the Mel-Temp apparatus. A Beckman Model DU Spectrophotometer was used for the ultraviolet spectra and a Beckman Model IR4 for the infrared. C, H analysis by Spang Microanalytical Laboratories, Ann Arbor, Mich. A Perkin-Elmer Model 154C Vapor Fractometer was used for chromatographic analysis.

Triphenylcarbethoxymethylphosphonium chloride dihydrate (II). Ethyl chloroacetate (34.7 g.; 0.28 mole) was added to a solution of triphenylphosphine (65.6 g.; 0.25 mole) in 50 ml. of benzene. The solution was swirled to mix, stoppered and set aside for one week. The crystals which formed were filtered, washed with ether and dried in air. Yield was 94.0 g (0.22 mole, 89%) of a white crystalline powder; m.p. 87–88° dec. (soften 86°). By recrystallization from a methylene chloride–carbon tetrachloride mixture, large prisms of unchanged melting point were obtained. The infrared spectrum had $\lambda_{\text{Nujol}}^{\text{max.}}$ 3521, 3448 cm.$^{-1}$ (bonded—OH) as well as the expected bands.

Anal. Calcd. for $C_{22}H_{22}ClO_2P\cdot 2H_2O$: C, 62.78; H, 6.23; P, 7.38; Cl, 8.43; H_2O, 8.55. Found: C, 63.02; H, 6.30; P, 7.31; Cl, 8.76, 8.31; H_2O (K. Fisher), 7.76, 7.75.

When an aliquot of the dihydrate was crushed and stored over phosphorus pentoxide at 2 mm. for one week, the m.p. was raised to 144° (dec.). When this dry material was stored in air for five days, its m.p. was 98° dec.

Dehydration of triphenylcarbethoxymethylphosphonium chloride dihydrate (II). Triphenylcarbethoxymethylphosphonium chloride dihydrate (21.04 g.; 50 mmoles) was added to 100 ml. of anhydrous benzene in a flask provided with a Dean-Stark trap and a nitrogen atmosphere. The flask was heated in a water bath and the solid melted to a yellowish oil. As boiling initiated, an unusual amount of frothing was observed. The gases (carbon dioxide) were passed through a barium hydroxide trap to form a copious white precipitate.

Boiling, under reflux, was continued for three hours, at the end of which time a lower layer with a constant volume of 1.3 ml. had collected in the trap and the oily material in the flask had solidified. The bath was removed and the reaction mixture was allowed to cool. The solid was isolated by filtration. The solid, its mother liquor, and the lower layer of the liquid in the Dean-Stark trap were worked up separately.

Solid. The solid was washed with anhydrous benzene and dried over paraffin shavings at 2 mm. An off-white solid was obtained; yield 15.67 g. (50 mmoles; 100%). Recrystallization from methylene chloride–carbon tetrachloride gave white crystals of triphenylmethylphosphonium chloride which were stored over phosphorus pentoxide at 2 mm. for two weeks; m.p. 217–218.5° (lit. 212–213°[5]; 222–224°[3]). The infrared spectrum of this material was in excellent agreement with that of an authentic specimen.[6]

Mother liquor. The mother liquor (benzene) from the filtration was analyzed by vapor phase chromatography and found to contain 0.73 g. of ethanol.

Trap liquid. The liquid in the lower layer of the Dean-Stark trap was found, by vapor phase chromatography, to consist of 0.78 g. of water and 0.53 g. of ethanol.

The yield of water was 0.78 g. (43 mmoles; 87%). The combined yield of ethanol was 1.3 g. (28 mmoles; 57%).

Acid hydrolysis of triphenylcarbethoxymethylphosphonium chloride dihydrate (II). Triphenylcarbethoxymethylphosphonium chloride dihydrate (4.21 g.; 10 mmoles) was dissolved in 200 ml. of 1% hydrochloric acid and set aside to evaporate. After three weeks, the sticky solid left in the casserole was dried over phosphorus pentoxide at 2 mm. The yield was 3.58 g. (10 mmoles; 100%). Two recrystallizations from absolute ethanol-ether gave 1.15 g. (3.2 mmoles; 32%) of white crystals; m.p. 219.5° dec. When mixed with authentic triphenylcarboxymethylphosphonium chloride[7] (m.p. 218° dec.), the melting point was 218.5° dec. The infrared spectrum was identical with authentic material.

Triphenylcarbethoxymethylene phosphorane (IV). *A.* Method of Isler[3] (from triphenylcarbethoxymethylphosphonium bromide). Triphenylphosphine condensed with ethyl bromoacetate to give the phosphonium bromide. Titration with sodium hydroxide gave triphenylcarbethoxymethylene phosphorane (V). Recrystallizations from ethyl acetate–hexane, benzene–petroleum ether, and then cyclohexane gave white prisms; m.p. 123.5–125.5° (lit. 116–117°[3]).

Anal. Calcd. for $C_{22}H_{21}O_2P$: C, 75.84; H, 6.08; P, 8.89. Found: C, 75.66; H, 6.12; P, 8.65.

The ultraviolet spectrum had $\lambda_{\text{max.}}^{95\%\text{EtOH}}$ 223 mμ, 267 mμ ($E_{1\text{ cm.}}^{1\%}$ 839, 114); [lit. $\lambda_{\text{max.}}^{95\%\text{ EtOH}}$ 222 mμ, 268 mμ ($E_{1\text{ cm.}}^{1\%}$ 865, 116[3])]. The infrared spectrum is remarkable in that it lacks any absorption in the carbonyl region, but rather has a strong absorption at 1672 cm.$^{-1}$

B. From triphenylcarbethoxymethylphosphonium chloride dihydrate (II). Triphenylcarbethoxymethylphosphonium chloride dihydrate (2.10 g.; 5 mmoles) was dissolved in 20 ml. of water. Phenolphthalein was added and the solution was made basic by the addition, during stirring, 0.5*N* sodium hydroxide to the end-point. The white crystalline

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(4) D. B. Denney and L. C. Smith, *Chem. & Ind.*, 290 (1961).

(5) A. Michaelis and H. v. Soden, *Ann.*, **229**, 295 (1885).

(6) Kindly supplied by Prof. D. B. Denney.

(7) D. B. Denney and L. C. Smith, *Chem. & Ind.*, 290 (1961). Sample supplied by Prof. D. B. Denney.

powder formed was isolated by filtration, washed thoroughly with water and dried in air. The yield was 1.74 g. (5 mmoles; 100%); m.p. 122.5-124.5—undepressed when admixed with authentic material as prepared under *A*. The infrared spectrum was the same as that of authentic.

Acid stability of triphenylcarbethoxymethylene phosphorane (IV). Triphenylcarbethoxymethylene phosphorane (0.348 g.; 1 mmole) was dissolved in 10 ml. of 10% hydrochloric acid. Immediately upon attaining a clear solution, the pH was adjusted to the phenolphthalein end-point with a 10% sodium hydroxide solution. The white solid which formed was filtered, washed with water and dried in air. It weighed 0.330 g. (0.95 mmole; 95%) and was shown to be starting material by a mixed melting point determination and the congruency of infrared spectra.

Acid hydrolysis of triphenylcarbethoxymethylene phosphorane (IV). Triphenylcarbethoxymethylene phosphorane (3.48 g.; 10 mmoles) was dissolved in 100 ml of 10% hydrochloric acid and set aside to evaporate. One month later, 3.55 g. (10 mmoles; 100%) of yellowish crystals were obtained. Two recrystallizations from absolute ethanol-ether gave 1.63 g. (4.6 mmoles; 46%) of white crystals; m.p. 218° dec. When mixed with authentic triphenylcarbethoxymethylphosphonium chloride (m.p. 219.5°), the melting point was 218.5° dec. The infrared spectrum was identical with authentic material.

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Bisulfite Adducts of Acrolein

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One molecular equivalent of sodium bisulfite reacts with acrolein to form a product which on hydrogenation and ring closure yields small amounts of 1,3-propanesultone.[1] As methacrolein and mesityl oxide by similar reactions yield 2-methyl-1,3-propanesultone[1] (3-oxy-2-methylpropane-1-sulfonic acid sultone), and 1,1,3-trimethyl-1,3-propanesultone,[2] both in good yield and as the mesityl oxide adduct is known to be sodium 2-methyl-4-pentanone-2-sulfonate[3]; it might be assumed that the acrolein product is also the double bond adduct, sodium propanal-3-sulfonate. In contrast, the reaction of cinnamaldehyde with one equivalent of sodium bisulfite yields the carbonyl adduct, sodium 3-phenyl-2-propene-1-hydroxy-1-sulfonate.[4]

We have now obtained evidence that the initial product of the reaction between acrolein and sodium bisulfite at *p*H below 5 is the unsaturated carbonyl adduct, sodium 1-hydroxy-2-propene-1-sulfonate. The addition of sodium bisulfite to the carbonyl group in this *p*H range is rapid and not strongly exothermic:

$$\mathrm{NaHSO_3 + CH_2{=}CH{-}CHO \longrightarrow CH_2{=}CH{-}CH(OH)SO_3Na}$$

This adduct, at *p*H below 5, slowly adds a second sodium bisulfite, yielding sodium 1-hydroxy-1,3-propane disulfonate:

$$\mathrm{CH_2{=}CH{-}CH(OH)SO_3Na + NaHSO_3 \longrightarrow NaSO_3{-}CH_2{-}CH_2{-}CH(OH)SO_3Na}$$

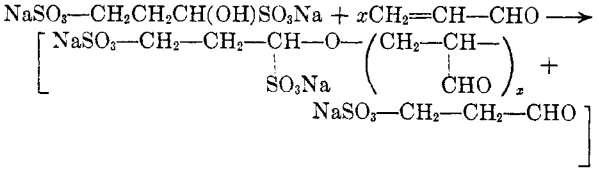
In the *p*H range above about 5.2 two reactions occur: The unsaturated carbonyl adduct disproportionates to the diadduct and a second mole of bisulfite adds either to the original unsaturated carbonyl adduct or to acrolein produced in the disproportionation. This reaction system is exothermic

$$\mathrm{2CH_2{=}CH{-}CH(OH)SO_3Na \longrightarrow NaSO_3{-}CH_2{-}CH_2{-}CH(OH)SO_3Na + CH_2{=}CH{-}CHO}$$

$$\mathrm{CH_2{=}CH{-}CH(OH)SO_3Na + NaHSO_3 \longrightarrow NaSO_3{-}CH_2{-}CH_2{-}CH(OH)SO_3Na}$$

$$\mathrm{CH_2{=}CH{-}CHO + 2\,NaHSO_3 \longrightarrow NaSO_3{-}CH_2{-}CH_2{-}CH(OH)SO_3Na}$$

As shown in the first equation above, the unsaturated carbonyl adduct alone disproportionates with evolution of heat at *p*H of about 5.2 or higher yielding the diadduct. In this case the expected amount of free acrolein is not obtained because acrolein reacts with the diadduct:



$$\mathrm{NaSO_3{-}CH_2CH_2CH(OH)SO_3Na + \mathit{x}CH_2{=}CH{-}CHO \longrightarrow \left[NaSO_3{-}CH_2{-}CH_2{-}\underset{SO_3Na}{CH}{-}O{-}\left(CH_2{-}\underset{CHO}{CH}{-}\right)_{\mathit{x}} + NaSO_3{-}CH_2{-}CH_2{-}CHO\right]}$$

This last reaction has been carried out independently using a neutral, aqueous solution of recrystallized sodium 1-hydroxy-1,3-propane disulfonate, and aqueous acrolein. The product probably contains a small amount of sodium propanal-3-sulfonate.

So far it has not been possible to isolate sodium 1-hydroxy-2-propene-1-sulfonate from water solution. The identification of the compound is based on examination of the water solution by NMR spectroscopy, on the Raman spectrum of the solution, on ultraviolet determination of residual acrolein, and on chemical analysis. These data indicate the presence of the $CH_2{=}CHR$ and $R{-}CH(OH)SO_3Na$ groups.

Sodium 1-hydroxy-1,3-propane disulfonate when treated with aqueous hydrochloric or sulfuric acid splits out sulfur dioxide yielding sodium propanal-

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(1) C. W. Smith, D. G. Norton, and S. A. Ballard, *J. Am. Chem. Soc.*, **75**, 748 (1953).

(2) J. Willems, *Bull. soc. chim. Belg.*, **64**, 432 (1955).

(3) A. Pinner, *Ber.*, **15**, 589 (1882).

(4) F. Heusler, *Ber.*, **24**, 1805 (1891).