Optically active 2-octyltrimethylammonium bromide was prepared from resolved 2-aminooctane in an identical manner. From 2-aminooctane, $\alpha^{24}D$ −2.377° (88.6% optically pure), the optically active salt obtained had $\alpha^{23}D$ +3.18° (*c* 1.0 *M* in methanol, 0.5 dm).

Cmc Determinations.—All solutions of the ammonium salts were prepared in "Lecktrostill Steam Distilled Water," resistivity >1.5 × 10^6 ohm cm (Electrified Water Co., Newark, N. J.). Stock solutions were water, 1.5 *M* aqueous NaBr, 1.5 *M* aqueous NaBr (acidified to pH 1.5 with HBr solution which had been preadjusted to 1.5 *M* in bromide ion), and 1.5 *M* and 2.0 *M* aqueous $NaClO_4$ (acidified to pH 1.5 with $HClO_4$). Solutions of the amine or the ammonium salt were prepared (above the cmc) using these stock solutions. 2-Octylamine solutions were preadjusted to pH 1.5 with aqueous HBr (1.5 *M* in bromide) before bringing to dilution with bromide stock solution. A similar procedure was used in the perchlorate experiments.

Surface tension was determined in a cell thermostatted at 31° by a Haake constant-temperature circulating pump. An aliquot of the amine or the ammonium ion solution (at a concentration above the cmc) was successively diluted by addition of 0.50-ml portions of the appropriate stock solution from an accurate buret (±0.01 ml). Stirring was accomplished after each dilution with a micro stirring bar and the surface tension corresponding to the then present concentration[20] was measured with a DuNuoy tensiometer.[21] Cmc values were then determined from graphs of observed surface tension *vs.* log (concentration). Average cmc values, determined from at least three separately prepared micellar solutions appear in Table I.

Registry No.—(±)-2-OA-Br, 25474-24-2; (−)-2-OA-Br, 25474-25-3; (±)-2-OTA-Br, 25474-26-4; (+)-2-OTA-Br, 25474-27-5; (±)-2-OA-ClO_4, 25474-28-6.

Acknowledgments.—We thank the National Institutes of Health (Gm-13585) and the National Science Foundation (GP-12645) for financial support.

(20) The volume additivity demanded by this procedure was demonstrated to ±0.01 ml by parallel control experiments for cases 1, 2, and 4 of Table I.

(21) The average deviation from the mean of a series of 12 surface tension readings taken either on water or a micellar solution was ±0.3 dynes/cm.

The Structure of the Adduct from Diphenylketene and Triethyl Phosphite

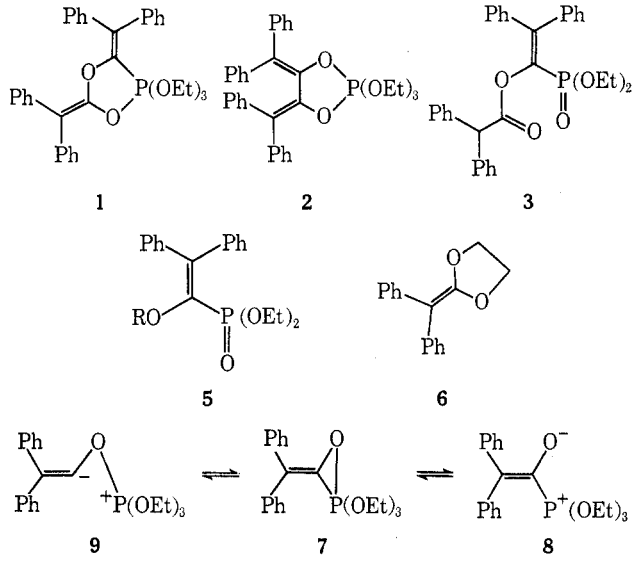
J. E. BALDWIN[1] AND J. C. SWALLOW

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received March 23, 1970

During the course of work on the interaction of trivalent phosphorus with carbonyl derivatives we have examined the 2:1 adduct of diphenylketene and triethyl phosphite.[2] The structure of this substance, which undergoes a high-temperature deoxygenation rearrangement to diphenylacetylene,[2] has been the subject of some speculation;[3] and we here describe a solution to this problem.

The adduct, $C_{34}H_{35}PO_5$, prepared as previously described[2] showed a medium strength band at 1660 cm^{-1} in the infrared (solid and solution) and the nmr spectrum, which contained only phosphorus-bound ethoxyl and aryl protons, underwent an irreversible change at 90°. In accordance with previous speculative suggestions for the presence of pentacoordinate phosphorus atom in this molecule, the ^{31}P magnetic resonance spectrum showed a chemical shift of +55 ppm relative to 85% H_3PO_4, without solvent dependence.[4] However "freezing out" of discrete pseudorotational structures could not be observed in the proton spectrum of the ethoxyl ligands down to −114°.[4,5] At this stage two structures, **1** and **2**, seemed in accord with the evidence, neither of which possessed a carbonyl function, *vide supra*. Distinction between these two possibilities was made on the basis of hydrolytic behavior, for in moist air or in wet ether the adduct was converted into the enol ester (**3**), ν_{max} 1760 cm^{-1}, and ethyl diphenylacetate (**4**). That **4** was a further ethanolysis product of **3**



was demonstrated by the observation that methanol, with a trace of sodium methoxide, converted **3** into methyl diphenylacetate. More vigorous hydrolysis of **3** gave almost 2 mol of diphenylacetic acid. Confirmation of the enol ester structure **3** was achieved by synthesis. Thus the Arbuzov product from diphenylacetyl chloride and triethylphosphite was the stable enol phosphonate (**5**, R = H), from its composition and positive ferric chloride test.[6] The enolic hydroxyl group of **5** (R = H), exchangeable with deuterium oxide, was acetylated to the acetate **5** (R = $COCH_3$), ν_{max} 1760 cm^{-1}, and methylated (diazomethane) to the ether **5** (R = CH_3). Treatment of **5** (R = H) with diphenylketene yielded the phosphonate **3**, identical in infrared, ultraviolet and nmr spectra with the originally isolated substance. The hydrolytic conversion of the adduct to **3** then enables the assignment **1** to be proposed for this substance and rejection of alternative **2**, since the latter could not readily yield an enol ester **3** under simple hydrolytic conditions. As a close ultra-

(1) Alfred P. Sloan Fellow, 1969–1970.

(2) T. Mukaiyama, H. Nambu, and M. Okamoto, *J. Org. Chem.*, **27**, 3651 (1962).

(3) R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press, New York, N. Y., 1965, p 197; A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, New York, N. Y., 1967, p 88.

(4) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).

(5) F. H. Westheimer, *ibid.*, **1**, 70 (1968).

(6) An analogous enolic compound has recently been described by Richard N. McDonald and Donald G. Hill, *Chem. Commun.*, **12**, 671 (1969).

violet model for the chromophore of **1** we prepared the glycol acetal (**6**) of diphenylketene which showed λ_{max} 272 mμ (ε 20,000) in reasonable accord with the broad maximum at 257 mμ (ε 40,000) noted for the adduct. The hypsochromic shift in **1** is apparently due to the presence of the pentavalent phosphorus in the five-membered ring. Whilst the detailed mechanisms of reaction of trivalent phosphorus with carbonyl groups is as yet unclear[4] a rationale of the formation of **1** may be obtained through the intermediacy of a initial 1:1 adduct (**7**), which in its open form (**8**) undergoes a simple 1,3 dipolar addition to another mole of ketene, providing the 1,4,2-dioxyphospholane structure **1**. We have observed no change in the ^{31}P chemical shift (chloroform solution) up to 90°, at which temperature an irreversible thermal decomposition takes place, thus eliminating an isomerization to a 1,3,2-dioxyphospholane structure **2**, as reported in some systems by Ramirez.[4] The thermolysis to acetylene is probably reversal of the last step followed by decomposition of **7** to dipole **9**. Decomposition of **9** to diphenylacetylene and triethylphosphate is a reaction which finds close analogy in the tolane synthesis.[7]

Experimental Section[8]

All reactions were performed under deoxygenated dried prepurified nitrogen. Melting points were measured on a Kofler hot stage and are uncorrected. Ultraviolet spectra were recorded on a Coleman-Hitachi 124 double-beam spectrometer. Infrared spectra were recorded on a Perkin Elmer 257 spectrophotometer. ^1H nmr spectra at room temperature were measured on a Varian A-60A spectrometer with tetramethylsilane as internal reference. Variable temperature ^1H and ^{31}P nmr spectra were obtained from a Varian HA-100 spectrometer equipped with a V6040 temperature control and a probe fitted with a thermocouple for measuring the temperature. In the HR mode at operating frequency 40.5 MHz ^{31}P nmr spectra were calibrated by the sideband technique using a Hewlett-Packard variable audiooscillator and P_4O_6 as external reference. Mass spectra were measured on a AEI MS9 mass spectrometer.

Adduct 1. 3,5-Bis(diphenylmethylene)-1,4,2-dioxatriethoxyphospholane.—Dry triethyl phosphite (0.912 g) reacted exothermally when added dropwise to freshly distilled diphenylketene (2.142 g) in 2 ml Et_2O. Evaporation yielded yellow crystalline 1: mp 85–100°; uv max (C_6H_{12}) 257 mμ (ε 40,000); ir (C_6H_6, C_6H_{12}, $CHCl_3$, CH_2Cl_2, Nujol) 1660 (C=C), 1600 cm^{-1}; ^1H nmr (CS_2) σ 0.85 (m, 6), 3.68 (m, 4), 7.15 (m, 20); ^{31}P nmr ppm relative to 85% H_3PO_4 (0 ppm) (C_6H_6, CH_2Cl_2, $CHCl_3$) +55; mass spectrum (70 eV) *m/e* (relative intensity) 240 (4), 182 (3), 167 (16), 105 (7), 77 (4).

Hydrolysis of Adduct.—Stirring in a moist air stream produced an oily product mixture. Separation by column chromatography (silica gel) gave **3** and ethyl diphenylacetate. **1** when stirred with wet ether under dry nitrogen gave the same products after evaporation and chromotography.

Methanolysis of 3.—A solution of **3** in MeOH containing a little sodium methoxide was refluxed for 2 hr. Evaporation yielded methyl diphenylacetate, recrystallized from EtOH: mp 57–58°; identical with an authentic specimen.

Hydrolysis of 3.—An ethereal solution of **3** (0.372 g) when stirred for 3 hr with 5 ml 4 *N* NaOH, acidified with HCl and extracted with Et_2O yielded diphenylacetic acid (0.257 g) upon evaporation: mp 140–143°; identical with an authentic specimen.

2,2-Diphenylethylenol-1-(ethyl)phosphonate (5) (R = H).—Triethyl phosphite (0.72 g) in 20 ml was added dropwise to a solution of diphenylacetyl chloride (1.0 g) in 30 ml Et_2O. The solution was refluxed under dry nitrogen for 3 hr. After solvent evaporation, the product was recrystallized from benzene and hexane: mp 99–103°; uv max (95% EtOH) 260 mμ (ε 20,000) with 1 drop 4 *N* NaOH 300 mμ; ir (Nujol) 3400–3100 (b, OH), 1490 (m, C=C), 1200 (b, P=O), 980 (b, P–O–C) after D_2O treatment and recrystallization 2500–2200 cm^{-1} (b, OD); ^1H nmr ($CDCl_3$) σ 1.15 (m, 6), 3.95 (m, 4), 6.72 (bs, 1) function of concentration, 7.31 (s, 10) after D_2O treatment broad singlet disappears; ^{31}P nmr (benzene) ppm relative to 85% H_3PO_4 −9; mass spectrum (70 eV) *m/e* (relative intensity) 332 (1), 304 (2), 194 (12), 167 (27), 137 (1).

Anal. Calcd for $C_{18}H_{21}O_4P$: C, 65.05; H, 6.37; P, 9.32. found: C, 64.91; H, 6.44; P, 9.48.

1-(Acetoxy)-2,2-diphenylethylene(ethyl)phosphonate (5) (R = $COCH_3$).—A solution of **5** (R = H) (1.20 g) in 25 ml Ac_2O plus a trace of NaOAc when heated at 40° for five hours yielded the crude oil after evaporation of excess Ac_2O. Purification of **5** (R = $COCH_3$) was accomplished by preparative tlc on alumina GF, eluted with $CHCl_3$: ir (neat) 1760 (s, C=O), 1260 (s), 1220 (b) 1130 (s), 1040 (b); nmr (CCl_4) σ 1.11 (m, 6), 1.93 (s, 3) 3.88 (m, 4) 7.20 (d, 10); mass spectrum (25 eV) *m/e* (relative intensity) 346 (18), 332 (15), 317 (10), 209 (10), 194 (61), 167 (26), 149 (10), 121 (10), 111 (10), 105 (16), 93 (10), 43 (24).

2,2-Diphenylethylene-1-(ethyl)phosphonate Methyl Ether (5) (R = CH_3).—An ethereal solution (27 ml) of CH_2N_2 (0.315 g) was added to **5** (R = H) (2.50 g). After stirring at 0° for 3 hr followed by evaporation of Et_2O, the oil **5** (R = CH_3) was isolated in 63% yield: uv max (C_6H_{14}) 260 mμ (ε 10,000); nmr (CCl_4) σ 1.05 (m, 6), 3.42 (s, 3), 3.85 (m, 4), 7.20 (m, 10); mass spectrum (25 eV) *m/e* (relative intensity) 346 (20), 317 (10), 209 (10), 167 (14), 121 (10). Although spectral properties were in full agreement with those expected for these new compounds, **5** (R = CH_3) (R = $COCH_3$), elemental analysis was not attempted.

1-(Diphenylacetoxy)-2,2-diphenylethylene(ethyl)phosphonate (3).—Triethylamine (1.12 g) in 15 ml C_6H_6 added dropwise into diphenylacetyl chloride (2.56 g) in 15 ml C_6H_6 generated diphenylketene in solution and Et_3NHCl. **5** (R = H) (3.70 g) in 20 ml C_6H_6 was added to above reaction mixture. After 10 hr at 60°, filtration and evaporation of C_6H_6 yielded the oil **3**. Purification was accomplished by column chromatography (silica gel) eluted with $CHCl_3$ followed by preparative tlc (silica gel GF254) doubly eluted with $CHCl_3$: uv max (C_6H_{14}) 257 mμ (ε 11,000); ir (neat) 3100–2900 (m, CH), 1760 (s, C=O), 1665 (w, C=C), 1600 (w), 1255 (b), 1110 (b), 1020 (b, P–O–C), 745 (s), 690 cm^{-1} (s); ^1H nmr (CCl_4) σ 1.03 (m, 6), 3.83 (m, 4), 4.95 (s, 1), 7.20 (m, 20); ^{31}P nmr (C_6H_6) ppm relative to 85% H_3PO_4 −7; mass spectrum (70 eV) 331 (1), 233 (8), 182 (108), 165 (27), 105 (268), 77 (186).

Anal. Calcd for $C_{32}H_{31}O_5P$: C, 72.99; H, 5.93; P, 5.88. Found: C, 73.00; H, 6.07; P, 5.66.

This material was identical in all spectral and chromatographic properties with the compound obtained by hydrolysis of **1**, *vide supra*.

Diphenylketene Ethylene Acetal (6).—This acetal was prepared by a modification of the procedure of Gulbins.[9] Instead of generating diphenylketene *in situ* from azibenzil, it was formed as described by Taylor.[10] The Et_3NHCl was filtered off, followed by addition of ethylene carbonate and a trace of LiCl. After 3.5 hr at 180°, distillation yielded the acetal which was recrystallized from C_6H_{14}: bp 150–155° (0.12 mm), mp 141–144° [lit. bp 174–175° (0.3 mm), mp 149–151°]; uv max (C_6H_{14}) 272 mμ (ε 20,000); ir (Nujol) 1650 (s, C=C), 1600 (w), 1050 cm^{-1} (sb, C—O—C); nmr ($CDCl_3$) σ 4.23 (s, 4), 7.25 (s, 10); mass spectrum (70 eV) 238 (9), 165 (15), 105 (4), 77 (3).

Registry No.—**1**, 25577-16-6; **3**, 25577-17-7; **5** (R = H), 25577-18-8; **5** (R = CH_3), 25577-19-9; **5** (R = $COCH_3$), 17474-77-0.

Acknowledgment.—We thank the Alfred Sloan Foundation and U. S. Public Health Service, and Eli Lilly and Company for support.

(7) A. A. Bothner-By, *J. Amer. Chem. Soc.*, **77**, 3293 (1955); J. G. Pritchard and A. A. Bothner-By, *J. Phys. Chem.*, **64**, 1271 (1960).

(8) Elemental analyses were performed by the Midwest Microlab Inc., Indianapolis, Ind. 46226.

(9) K. Gulbins and K. Hamann, *Chem. Ber.*, **94**, 3287 (1961).

(10) Reported in L. F. Fieser and M. Fieser, "Reagents for Organic Syntheses," Wiley, New York, N. Y., 1967, p 344.