(s, 3, CH_3C=), 2.14 (s, 3, aromatic CH_3), 2.1, 2.8 (m, 4, J = 7 Hz, CH_2CH_2), 6.39 (s, 1, CH=C), 7.07 (s, 1, aromatic); mass spectrum m/e 252 (M^+). *Anal.* Calcd for $C_{12}H_{13}BrO$ (253.14): C, 56.93; H, 5.18; Br, 31.57. Found: C, 57.19; H, 5.28; Br, 31.68.

The second fraction gave on concentration to dryness and vacuum distillation at 120° (0.05 mm) 36 mg (7%) of **9**: mp 159–162°; nmr ($CDCl_3$) δ 2.37 (s, 3, aromatic CH_3), 2.42 (s, 3, aromatic CH_3), 7.00 (s, 1, aromatic), 7.17 (d of d, J_{meta} = 2, J_{ortho} = 8 Hz, aromatic), 7.45 (d, 1, J_{meta} = 2 Hz, aromatic), 7.51 (d, 1, J_{ortho} = 8 Hz, aromatic); mass spectrum m/e 172 (M^+). *Anal.* Calcd for $C_{12}H_{12}O$ (172.22): C, 83.69; H, 7.02. Found: C, 83.37; H, 6.95.

The third fraction gave on evaporation a 100% yield of ketone **3**.[1]

Oxidation of Ketone 3 to 2-Ethyl-4-methyl-2-(1,4-dioxo-1-hexyl)-5-(4-oxo-3-hexyl)tetrahydrofuran (12) and 2-Ethyl-4-methyl-2-(1-acetoxy-4-oxohexyl)-5-(4-oxo-3-hexyl)tetrahydrofuran (13).—To a solution of 9.16 g (27 mmol) of ketone **3** in 150 ml of acetone was added 25 ml of Jones reagent[6] over 1 hr at room temperature. After a further 16 hr, the reaction solution was diluted with 500 ml of water and extracted with three 500-ml portions of methylene chloride. The pooled extract was washed with aqueous $NaHCO_3$, dried (Na_2SO_4), and concentrated under reduced pressure to 8.6 g of an oil. The oil was chromatographed on 400 g of silica gel using a gradient from 1 l. of 1:1 methylene chloride–hexane to 1 l. of methylene chloride followed by a second gradient from 4 l. of methylene chloride to 4 l. of 2:3 methylene chloride–ether. A fraction eluted after 4 l. of solvent had passed through the column gave on evaporation 1.38 g (16%) of **12**: $[\alpha]_D$ −12.6° (c 1, CH_3OH); ir ($CHCl_3$) 1720 cm^{-1} (CO); uv max (2-propanol) 285 nm (ε 127); mass spectrum m/e 323 (M − 1), 309 (M − CH_3), 295 (M − C_2H_5), 211 (M − 113); nmr ($CDCl_3$) δ 2.50 (m, 8, 4 CH_2CO), 3.60 (m, 1, CHOC). *Anal.* Calcd for $C_{19}H_{32}O_4$ (324.45): C, 70.33; H, 9.94. Found: C, 70.11; H, 9.65.

Immediately following **12**, a second fraction was eluted which on evaporation gave 3.83 g (37%) of **13**: $[\alpha]_D$ +20° (c 1, CH_3OH); ir ($CHCl_3$) 1715 (ketone), 1730 cm^{-1} (ester); uv max (2-propanol) 281 nm (ε 80); mass spectrum m/e 368 (M^+), 339 (M − C_2H_5), 308 (M − $C_2H_4O_2$), 211 (M − 157); nmr ($CDCl_3$) δ 2.05 (s, 3, CH_3CO), 3.49 (m, 1, CHOC), 4.97 (d of d, 1, $CH_2CHOCOCH_3$, J = 4, 9.5 Hz). *Anal.* Calcd for $C_{21}H_{36}O_5$ (368.50): C, 68.44; H, 9.85. Found: C, 68.73; H, 9.65.

Preparation of 2-Ethyl-4-methyl-2-(1-hydroxy-4-oxo-1-hexyl)-5-(4-oxo-3-hexyl)tetrahydrofuran (14).—To a solution of 1.41 g (3.8 mmol) of acetoxy acetone **13** in 25 ml of methanol was added 19 ml of 10% aqueous NaOH. The reaction mixture was stirred for 18 hr at room temperature and then diluted with 50 ml of water and extracted with three 50-ml portions of ethyl acetate. The extracts were combined, dried (Na_2SO_4), and evaporated to an oil. Distillation of the oil gave 1.2 g (96%) of **14**: bp 170° (0.05 mm); $[\alpha]_D$ +18° (c 1, CH_3OH); ir ($CHCl_3$) 1715 (ketone), 3630 cm^{-1} (OH); uv max (2-propanol) 278 nm (ε 102); mass spectrum m/e 326 (M^+), 308 (M − H_2O), 211 (M − 115); nmr ($CDCl_3$) δ 3.55 (m, 1, CHOC), *no* $CHOCOCH_3$. *Anal.* Calcd for $C_{19}H_{34}O_4$ (326.46): C, 69.90; H, 10.50. Found: C, 69.64; H, 10.52.

Preparation of 2-Ethyl-4-methyl-2-(2-ethyl-2-hydroxycyclohex-5-enon-5-yl)-5-(4-oxo-3-hexyl)tetrahydrofuran (16).—To a solution of 484 mg (1.37 mmol) of ketone **3** in 25 ml of acetone was added 1.8 ml of Jones reagent[6] over 1 hr at room temperature. After a further 16 hr, the reaction was diluted with 100 ml of water and extracted with three 100-ml portions of methylene chloride. The extracts were pooled, washed with aqueous $NaHCO_3$, dried (Na_2SO_4), and concentrated under reduced pressure to 450 mg of an oil. Without further purification the oil was dissolved in 10 ml of methanol and hydrolyzed using 5 ml of 10% aqueous NaOH. After 18 hr at room temperature the reaction was acidified with 1 N HCl and extracted with methylene chloride to give 378 mg of oily product. This product was then chromatographed on 150 g of silica gel using a gradient from 2 l. of methylene chloride to 2 l. of 9:1 methylene chloride–ether. After 2.7 l. of solvent had passed through the column, a uv-absorbing fraction was collected. Evaporation under reduced pressure gave 112 mg (23%) of **16** as a colorless oil: ir ($CHCl_3$) 1670 (C=CCO), 1710 cm^{-1} (CO); uv max (CH_3OH) 238 nm (ε 10,950); nmr ($CDCl_3$) δ 3.58 (m, 1, CHOC), 3.63 (s, 1, OH), 6.14 (s, 1, C=CHCO); mass spectrum m/e 350 (M^+), 335 (M − CH_3), 332 (M − H_2O), 321 (M − C_2H_5), 211 (M − 139). *Anal.* Calcd for $C_{21}H_{34}O_4$ (350.48): C, 71.96; H, 9.78. Found: C, 72.22; H, 9.84.

Acknowledgment.—We are indebted to the Physical Chemistry Department, Hoffmann-La Roche Inc., Nutley, N. J., under the supervision of Dr. R. P. W. Scott, for the analytical and spectral data.

Registry No.—**1a**, 25999-31-9; **1b**, 38784-08-6; **3**, 31478-26-9; **5**, 40919-48-0; **6**, 40919-49-1; **8**, 40919-50-4; **9**, 40919-51-5; **10**, 40919-52-6; **11**, 40919-53-7; **12**, 40919-54-8; **13**, 40919-55-9; **13**, 40919-55-9; **14**, 40919-56-0; **16**, 40919-57-1.

Synthesis of 2,4,6-Triphenyl-1,4-oxazine

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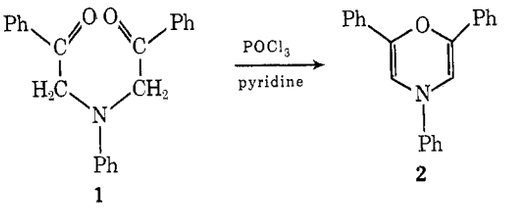
Although monocyclic 1,4-oxazines are known, only those with an oxygen or nitrogen substituent on the oxazine ring have been prepared.[1] In pursuing studies on the reactions of diphenacylaniline (**1**), the synthesis of a relatively stable, simply substituted oxazine was visualized. Thus, reaction of diphenacylaniline with an excess of $POCl_3$ in pyridine resulted in the formation of a red, crystalline compound with the proposed structure, 2,4,6-triphenyl-1,4-oxazine (**2**).



1 **2**

The oxazine formation can be explained easily by postulating a hemiketal intermediate which undergoes dehydration.

The structure of **2** is based on its analysis, spectral data, and chemical properties. The ir and nmr spectra are particularly informative. In addition to the usual aromatic absorption in the infrared, compound **2** has an intense peak at 1640 cm^{-1}, consistent with the vinyl ether–enamine structure.[2] The nmr spectrum provides additional evidence: a two-proton singlet at δ 6.44 (olefinic hydrogens); a one-proton multiplet centered at δ 6.83 (para hydrogen on aniline moiety); a two-proton multiplet centered at δ 6.95 (ortho hydrogens on aniline moiety); and a 12-proton multiplet centered at δ 7.30 (aromatic hydrogens). The uv spectrum, with absorption at 238 and 348 nm and a weak band at 440 nm, indicates some interaction of the oxazine double bonds with the attached aromatic rings.

The synthesis of **2** proceeded in good yield to give a moderately pure compound, but removal of a remaining impurity, which may be a decomposition prod-

(1) *Cf.*, *e.g.*, G. T. Newbold, F. S. Spring, and W. Sweeny, *J. Chem. Soc.*, 909 (1950); W. Paterson and G. R. Proctor, *Chem. Ind. (London)*, 254 (1961).

(2) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958, p 41.

uct, was difficult. Only by repeated recrystallizations from alcohol under nitrogen was an analytically pure sample obtained. The oxazine was stable in the solid state, but was unstable in certain solutions (*e.g.*, benzene or hexane), particularly in the presence of oxygen. No pure compounds have been isolated from this decomposition.

Compound **2** was unreactive toward $NaBH_4$ and reacted only partially with $LiAlH_4$ in pyridine or boiling alcoholic KOH. As expected, reaction with acid occurred readily. However, acid hydrolysis did not result in the expected regeneration of starting material. Instead, under a variety of conditions, the only substance isolated was a high molecular weight compound of complex structure.

The evidence at hand does not allow a definite structure for this compound or a mechanism for its formation. However, the compound was shown not to arise from diphenacylaniline, since, under the same conditions in which **2** was hydrolyzed (boiling acetic acid), diphenacylaniline reacted only partially and did not produce any of the hydrolysis product. The reactions of **2** will be the subject of future investigations.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Spectral data were obtained from a Perkin-Elmer Model 137 ir spectrophotometer, a Varian A-60 nmr spectrometer, and a Hitachi Perkin-Elmer Model 139 uv–visible spectrophotometer. Analyses were performed by the Chemical Analytical Services, Berkeley, Calif.

Diphenacylaniline (1).—A mixture of 3.00 g (15 mmol) of phenacyl bromide, 15 ml of 95% ethanol, 3.15 g of Na_2CO_3, and 0.60 ml (7.5 mmol) of aniline was stirred and heated under reflux for 3 hr. After cooling to room temperature, the solid was filtered and triturated with H_2O for 15 min, then refiltered and recrystallized from pyridine to give 1.40 g (57%) of **1**: mp 237–239° (lit.[3] mp 236–240°); uv λ_{max} (dioxane) 252 nm (ϵ 26,600), 282 (3600); ir 1680 cm^{-1} (Nujol mull).

2,4,6-Triphenyl-1,4-oxazine (2).—A mixture of 1.55 g (4.7 mmol) of **1** and 0.87 ml (9.4 mmol) of $POCl_3$ in 30 ml of pyridine (dried over CaH_2) was heated with occasional swirling at 100° for 45 min. The deep red solution was poured onto 50 ml of crushed ice and the resulting solid was filtered. Two recrystallizations from isopropyl alcohol gave 0.81 g (55%) of red needles, mp 167–180°. This material was 80–90% pure and contained an impurity with a carbonyl peak at 1680 cm^{-1}. Use of a nitrogen atmosphere for the reaction did not materially affect the yield or purity of the product. However, repeated recrystallization from alcohol under nitrogen gave a small amount (72 mg) of an analytically pure sample: mp 183–185°; uv (EtOH) λ_{max} 238 nm (ϵ 19,800), 348 (20,400), 440 (3100); ir (CS_2) strong absorption at 1640, 1250, 1040, 750, and 685 cm^{-1}; nmr (CS_2) δ 6.44 (s, 2 H), 6.83 (m, 1 H), 6.95 (m, 2 H), 7.30 (m, 12 H). *Anal.* Calcd for $C_{22}H_{17}NO$: C, 84.85; H, 5.51; N, 4.50. Found: C, 84.68; H, 5.40; N, 4.71.

Acid Hydrolysis of 2.—A mixture of 298 mg (0.96 mmol) of **2**, 35 ml of 95% ethanol, and 4 ml of concentrated HCl was heated to reflux for 30 min. The light yellow solid, which formed on cooling, was filtered and crystallized from 40% isopropyl alcohol–cyclohexane to give 71 mg (0.125 mmol) of colorless crystals with a waxy appearance, mp 231–234°. Recrystallization gave crystals: mp 236–238° uv (EtOH) λ_{max} 240 nm (sh, ϵ 17,200), 330 (36,500); ir (CS_2) strong absorption at 1655, 1240, 755, and 690 cm^{-1}; nmr (CS_2) δ 6.50 (m, 2 H), 6.75 (m, 4 H), 7.14 (m, 24 H). *Anal.* Calcd for $C_{40}H_{30}N_2O_2$: C, 84.19; H, 5.30; N, 4.91; mol wt, 572. Found: C, 84.39; H, 5.44; N, 4.76; mol wt 545 (Rast).

Registry No.—**1**, 41120-12-1; **2**, 41120-13-2; phenacyl bromide, 532-27-4; aniline, 62-53-3.

(3) G. K. Almstrom, *Justus Liebigs Ann. Chem.*, **411**, 350 (1916).

A Double Perkow Reaction. 1,3-Butadiene-2,3-diol Bis(dialkyl phosphate)

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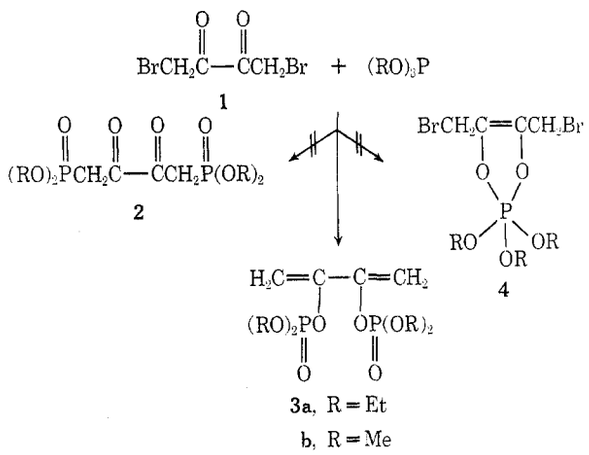
Trialkyl phosphites are known to react with α-halo ketones to yield β-ketophosphonates and/or vinyl phosphates (Arbuzov[1] and Perkow[2] products, respectively) and with nonhalogenated ketones and α diketones to yield phosphoranes.[3] In view of these results, an examination of the reactions of trialkyl phosphites with 1,4-dibromo-2,3-butanedione (**1**) was of interest. This ketone is capable of yielding all of these types of product, *i.e.*, phosphonates (**2**), phosphates (**3**), and phosphoranes (**4**), and allows an assessment of the competition between the three processes.



The addition of 2 mol of triethyl phosphite to a 1 *M* ethereal solution of **1** gave **3a** (98%) in an exothermic reaction. The ir spectrum of **3a** exhibited a characteristic olefinic stretching band (1602 cm^{-1}), but was transparent in the carbonyl region. The ^1H nmr spectrum consisted of a methyl triplet at τ 8.70, a methylene octet at 5.88, and a vinyl multiplet at 4.82. A broadened quintet at +6.8 ppm was observed in the ^{31}P nmr spectrum. These data are only consistent with structure **3a** and are inconsistent with either structure **2** or **4**. Similar results were obtained in the reaction of **1** with trimethyl phosphite; the ir and nmr data obtained for **3b** were similar to those cited for **3a**.

Further evidence for the proposed structure was provided by the absorption of 2 equiv of hydrogen by **3b** (atmospheric pressure, Pd/C). Reduction of the ethyl analog **3a** was inexplicably more difficult but was accomplished at 60 psi in methanol using 5% Ru/C–

(1) (a) G. M. Kosolapoff, "Organo-Phosphorus Compounds," Wiley, New York, N. Y., 1950; (b) P. C. Crofts, *Quart. Rev., Chem. Soc.*, **12**, 341 (1958); (c) M. Grayson and E. J. Griffith, "Topics in Phosphorus Chemistry," Wiley, New York, N. Y., 1964; (d) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, London, 1965.

(2) (a) F. W. Lichtenthaler, *Chem. Rev.*, **61**, 607 (1961); (b) P. A. Chopard, V. M. Clark, R. F. Hudson, and A. J. Kirby, *Tetrahedron*, **21**, 1961 (1965).

(3) (a) F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964); (b) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).