Experimental Section

All melting points, from a Mel-Temp capillary melting point apparatus, were corrected. Microanalyses were performed by Midwest Microlaboratories, Inc., Indianapolis, Ind. Infrared spectra were recorded with a Perkin-Elmer Model 137 Infracord. The nmr spectra were recorded on a Varian Model A-60 spectrometer, employing tetramethylsilane as an internal standard. Molecular weights were determined in chloroform on a Mechrolab vapor pressure osmometer, Model 301A.

Preparation of 6,7,8,9-Tetrahydro-2H-benz[*cd*]azulen-2-one (2).—A stirred, heterogeneous mixture of 22.7 g (0.1 mol) of **3**[9] and 150 ml of 15% hydrochloric acid solution was refluxed for 26 hr. After 4 hr a brown oil began to form on the acidic solution surface and, at the completion of the reflux period, this oil was separated and extracted with acetone. The orange insoluble material was filtered and recrystallized from dimethylformamide as dark yellow prisms (52%, based on weight recovery), mp >320°. This product was assumed to be a polymeric material of simplest empirical formula $C_{95}H_{80}N_5O_6$ (on basis of analysis).

Upon addition of water to the acetone extract, a second product was obtained which was filtered and recrystallized from benzene–hexane as light yellow plates. This material was identical with that substance which sublimed in the reflux condenser during the hydrolysis. Upon sublimation of this material *in vacuo* [82° (0.25 mm)], light yellow plates (20%, based on weight recovery), mp 88–90°, were obtained: $\lambda_{\max}^{\mathrm{KBr}}$ 3.44 (CH), 5.92 (C=O), 6.28 μ (C=C); nmr ($CDCl_3$) δ 1.72–2.55 (4 H, m), 2.83–3.17 (4 H, m), 5.92 (1 H, s), 7.03–7.62 (3 H, m).

Anal. Calcd for $C_{13}H_{12}O$: C, 84.78; H, 6.52; O, 8.88; mol wt, 184. Found: C, 84.61; H, 6.86; O, 8.84; mol wt, 186.

Compound **2** was also obtained by subjecting the initial brown oil to sublimation *in vacuo* at 82° (0.25 mm).

Preparation of Dimer 5a.—A yellow, homogeneous solution of 2.27 g (0.01 mol) of **3** in 50 ml of 15% sodium hydroxide solution was refluxed for 5 days with stirring (NH_3 evolution). After about 6 hr, a yellow material began to precipitate. At the conclusion of the reflux period the product was collected and recrystallized from ethyl acetate (42%), mp 252°, as white plates which could also be sublimed *in vacuo* [212° (0.3 mm)]: $\lambda_{\max}^{\mathrm{KBr}}$ 3.41 (CH), 3.49 (CH), 5.82 (C=O), 6.19 μ (C=C); nmr ($CDCl_3$ δ 1.25–3.19 (16 H, m), 3.90 (1 H, s), 4.14 (1 H, t), 7.08–7.58 (6 H, m).

Anal. Calcd for $C_{26}H_{24}O_2$: C, 84.78; H, 6.52; O, 8.88; mol wt, 368. Found: C, 85.05; H, 6.38; O, 8.71; mol wt, 358.

The reddish ethyl acetate mother liquor was evaporated and yielded a product which was sublimed *in vacuo* [82° (0.25 mm)], mp 88–90°, as light yellow needles (8%). This lower melting product was found to be identical with **2** by comparison with an authentic sample using thin layer chromatography employing ether–cyclohexane in a 1:1 ratio, and by comparison of ir spectra.

Catalytic Reduction of 5a.—A solution of 1.0 g (3.0 mmol) of **5a** in 100 ml of absolute ethanol was shaken with 0.8 g of platinum oxide in an atmosphere of hydrogen for 4 hr, after which the catalyst was removed and washed with warm ethanol. The ethanol mother liquors were combined and evaporated under a stream of air, leaving a white crystalline residue of **6** recrystallized from methanol as cream prisms (70%): mp 187–189°; $\lambda_{\max}^{\mathrm{KBr}}$ 3.40 (CH), 3.49 (CH), 5.87 μ (C=O). Quantitative hydrogenation indicated an uptake of 1 mol of hydrogen.

Anal. Calcd for $C_{26}H_{26}O_2$: C, 84.32; H, 7.03; O, 8.64; mol wt, 370. Found: C, 84.22; H, 7.05; O, 8.92; mol wt, 367.

Bromination of 5a.—A solution of 1.84 g (5.0 mmol) of **5a** in 320 ml of glacial acetic acid was stirred briefly at 0° before the dropwise addition of 1.60 g (0.01 mol) of Br_2 in 10 ml of glacial acetic acid. The addition to the stirred, cold acetic acid solution required 15 min. After stirring at room temperature for 1 hr, the red solution was poured over ice and the resulting aqueous solution was allowed to stand overnight, yielding a yellow product (67%). The product was collected by filtration, washed with water, and recrystallized from tetrahydrofuran–water as white needles: mp 182–182.5°; $\lambda_{\max}^{\mathrm{KBr}}$ 3.41 (CH), 3.51 (CH), 5.87 (C=O), 6.22 μ (C=C); nmr (CF_3COOH) δ 1.70–2.38 (14 H, m), 4.00 (1 H, s), 5.15 (1 H, s),[11] 7.12–7.78 (6 H, m).

Anal. Calcd for $C_{26}H_{22}O_2Br_2$: C, 59.32; H, 4.18; Br, 30.39; mol wt, 526. Found: C, 59.33; H, 4.50; Br, 29.89; mol wt, 522.

Extraction of the aqueous mother liquor with three 50-ml portions of chloroform followed by drying of the extracts with anhydrous calcium chloride, filtration, and evaporation yielded no additional products.

Registry No.—2, 17791-29-6; **5a**, 17791-30-9; **5b**, 17791-31-0; **6**, 17818-08-5.

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An Unusual Coupling of Cyclohexenone Cyclic Ketals

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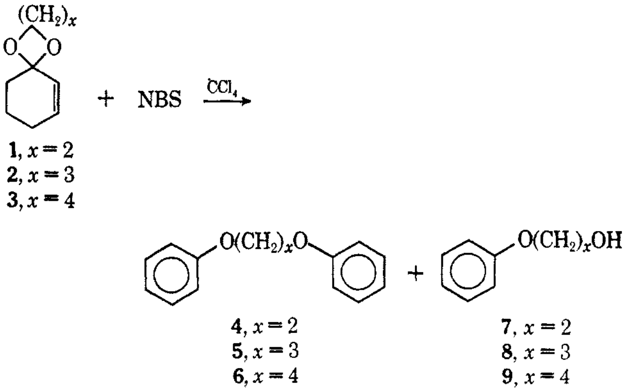
In a recent Note,[1] the preparation of 4-bromo-2-cyclohexenone ethylene ketal was reported as arising from the reaction of 2-cyclohexenone ethylene ketal and N-bromosuccinimide (NBS), using azobisisobutyronitrile and ultraviolet (uv) light as catalysts. When the reaction between 2-cyclohexenone ethylene ketal and NBS which had been recrystallized from water was carried out, a dramatically different result was obtained.



1, $x = 2$
2, $x = 3$
3, $x = 4$

4, $x = 2$
5, $x = 3$
6, $x = 4$

7, $x = 2$
8, $x = 3$
9, $x = 4$

When cyclic ketal **1** was treated with 1 equiv of NBS in refluxing carbon tetrachloride, a vigorous exothermic reaction occurred after only several minutes. Removal of the succinimide and evaporation of the solvent left a material whose ir spectrum showed strong absorption at 8.05, 13.36 and 14.45 μ. Elution chromatography of the crude reaction mixture yielded a white,[2] crystalline compound (**4**) and a much smaller amount of a colorless oil (**7**), bp 68–70° (3 mm). Compound **4** displayed the following: a mass spectrum with the parent peak at *m/e* 214 and intense fragments at *m/e* 121 and 107; uv absorption maximum at 220 mμ with weak absorption at 270 and 277 mμ; and pertinent ir bands at 6.26, 6.71, 8.05, 11.31, 12.54, 13.36 and 14.45 μ. The nmr spectrum of **4** displayed signals at δ 4.25 (2 H, s), 6.84 (3 H, m), and 7.25 (2 H, m). The melting

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[1] M. Graff and W. H. Gilligan, *J. Org. Chem.*, **32**, 3203 (1967).

[2] This material darkened slowly upon standing, probably indicating the presence of a small quantity of a presently unidentified bromine-containing material.

point of the material was 93-94° (lit.[3] mp 95°) after two crystallizations from ethanol.

The identification of **4** as 1,2-diphenoxyethane and **7** as 2-phenxoyethanol were made by comparison of their spectral and physical properties with those of authentic samples.

The formation of symmetrical bisphenoxylakanes was shown to be general in that cyclic ketals **2** and **3** reacted under the same conditions to yield 1,3-diphenoxypropane (**5**) and 1,4-diphenoxybutane (**6**), respectively, spectral properties of which are given in Table I.

TABLE I

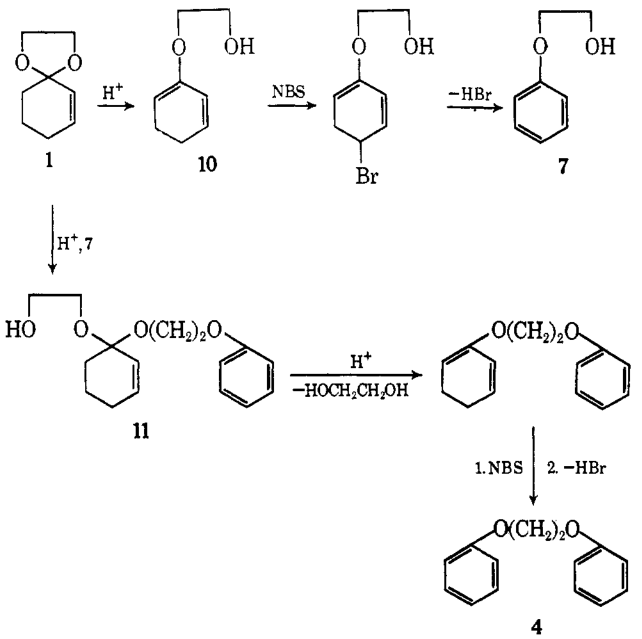
SPECTRAL PROPERTIES OF 1,3-DIPHENOXYPROPANE (5) AND 1,4-DIPHENOXYBUTANE (6)

Compd	Mass spectra, m/e	Uv, mμ	Ir, μ	Nmr, δ
5	228	221[a]	6.27, 11.45	2.21 (1, H, t)
	135	272	6.71, 12.30	4.10 (2 H, t)
	107	279	8.05, 13.30	6.79 (3 H, m)
			8.47, 14.49	7.24 (2 H, m)
6	242	220[a]	6.28, 11.42	1.93 (2 H, m)
	149	270	6.71, 12.00	3.94 (2 H, m)
	107	227	8.03, 13.39	6.77 (3 H, m)
			8.54, 14.52	7.19 (2 H, m)

[a] Maximum.

A possible coupling mechanism (Scheme I) involves opening of the cyclic acetal[4] to yield diene **10**, followed by bromination, and dehydrobomination to give 2-phenoxyethanol (**7**). This alcohol (**7**) reacts with **1** to form a new acetal (**11**) which upon protonation, elimination of ethylene glycol, bromination, and dehydrobromination yields 1,2-diphenoxyethane (**4**).

SCHEME I



The necessity of rigorously excluding moisture from allylic brominations of ethylene ketals has been previously noted[5] when an anomolous result was obtained with 2-cyclopentenone ethylene ketal and NBS.

Experimental Section

The ketals used in this work were prepared by the method of Salmi[6] from 2-cyclohexenone and the appropriate diol.

The NBS used was purchased from Matheson Coleman and Bell. It was recrystallized from water and dried in the air on a porous plate.

Reaction of 1 with NBS.—2-Cyclohexenone ethylene ketal (**1**, 1.4 g, 0.01 mol) and 1.8 g (0.01 mol) of NBS were placed in 12.5 ml of carbon tetrachloride. The reaction mixture was heated to reflux, and after only 5 min a vigorous exotherm occurred. Heating was continued for an additional 10 min before the solution was cooled and the succinimide was removed by filtration. Removal of the solvent left 1.2 g of a white solid. Elution chromatography of this material with 90% petroleum ether-10% benzene from 20 g of Woelm aluminum oxide (activity grade III) yielded 0.85 g of 1,2-diphenoxyethane (**4**) and 0.30 g of 2-phenoxyethanol (**7**).

Registry No.—**4**, 104-66-5; **5**, 726-44-3; **6**, 3459-88-9; **7**, 122-99-6.

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(5) C. H. DePuy, B. W. Ponder, and J. D. Fitzpatrick, *J. Org. Chem.*, **29**, 3508 (1964).

(6) E. J. Salmi, *Ber.*, **71**, 1803 (1938).

Reaction of Phosphoranes with Mannich Bases. Synthesis of α-Substituted β-Arylacrylic Acids *via* the Wittig Reaction

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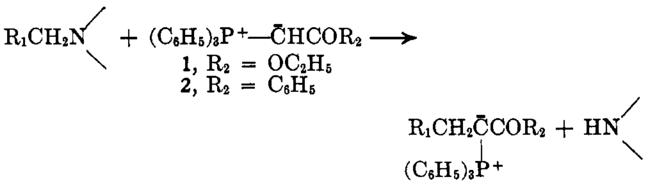
The alkylation of phosphonium ylides[1-3] is an important route to more complex ylides which are often unavailable by other methods.[4] Our continuing interest in carbon-carbon bond formation by amine replacement[5,6] led us to investigate the alkylation of phosphoranes with Mannich bases, and the synthetic utility of the products of this reaction.

Carbethoxymethylenetriphenylphosphorane (**1**) and benzoylmethylenetriphenylphosphorane (**2**) were found to react readily with Mannich bases according to Scheme I.

SCHEME I



$$R_1CH_2N\langle + (C_6H_5)_3P^+\!-\!\bar{C}HCOR_2 \longrightarrow R_1CH_2\overset{-}{\underset{(C_6H_5)_3P^+}{C}}COR_2 + HN\langle$$

$$\mathbf{1},\ R_2 = OC_2H_5 \qquad \mathbf{2},\ R_2 = C_6H_5$$

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(1) G. Wittig and M. Rieber, *Ann.*, **562**, 177 (1949).

(2) H. J. Bestmann and H. Schultz, *Tetrahedron Lett.*, No. 4, 5 (1960).

(3) H. J. Bestmann and H. Schultz, *Ber.*, **95**, 2921 (1962).

(4) For a recent review of reactions of phosphonium ylides, see A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966.

(5) M. von Strandtmann, M. P. Cohen, and J. Shavel, Jr., *J. Org. Chem.*, **30**, 3240 (1965).

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