TABLE I

ALLYLOXYALKANOLS

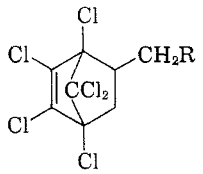
$CH_2{=}CHCH_2OR$

Substituent R	B.P.°	mm.	n_D^{25}	Literature Values B.P.°	mm.	n_D
CH_2CH_2OH	56	10	1.4326	159–160	atm	1.4355(20)[a]
				58–60	20	1.4360(20)[b]
$(CH_2CH_2O)_2H$	106	10	1.4445	98–101	2	1.4440(20)[a]
$CH_2CHOHC_2H_5$	95	60	1.4312	. . .	. . .	. . . [c]
$CH_2CH(C_6H_5)OH$	125	10	1.5193	118–119	4.5	1.5167(30)[d]

[a] A. A. Berlin, A. K. Dubagova, and E. F. Rodionova, *Sbornik Statei Obshchei Khim*, **2**, 1560 (1953); *Chem. Abstr.*, **49**, 5388 (1955). [b] V. N. Kotreelev and I. K. Rubstova, *Khim Prom.*, **1953**, 8; *Chem. Abstr.*, **50**, 6384 (1956). [c] *Anal.* Calcd. for $C_7H_{14}O_2$: C, 64.59; H, 10.84. Found: C, 63.91; H, 10.35. [d] D. Swern, G. N. Billen, and H. B. Knight, *J. Am. Chem. Soc.*, **71**, 1152 (1949).

TABLE II

(1,4,5,6,7,7-HEXACHLOROBICYCLO[2.2.1]-5-HEPTEN-2-YL)METHOXYALKANOLS[a]



Substituent R	Yield, %	B.P.°	mm	n_D^{25}	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Chlorine Calcd.	Chlorine Found
OCH_2CH_2OH	72	167	0.3	1.5446	32.03	31.75	2.69	2.51	56.74	57.40
$O(CH_2CH_2O)_2H$	75	185	0.2	1.5335	34.40	34.29	3.37	3.43	50.78	50.55
$OCH_2CHOHC_2H_5$	62	164	0.2	1.5319	35.76	36.21	3.50	3.49	52.79	52.80
$OCH_2CH(C_6H_5)OH$	42	250	0.8	1.5673	42.61	41.97	3.13	3.37	47.17	47.60

[a] Elemental analyses by Dr. S. A. Shrader, Analytical Laboratories, The Dow Chemical Co., Midland, Mich.

biological screening against *S. aureus* whereas the 2-allyloxy-1-phenylethanol adduct shows little or no activity in any of the three latter tests.

EXPERIMENTAL

Typical preparative details are given for only one experiment; the other compounds were prepared under nearly identical conditions (Tables I and II).

Preparation of (2-(1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-5-hepten-2-yl)methoxyethoxy)ethanol. A mixture of 146 g. (1 mole) of 2-(2-allyloxyethoxy)ethanol (see Table I for physical data on starting compounds), 272 g. (1 mole) of hexachlorocyclopentadiene and 500 ml. of *o*-xylene was placed in a 2-l., single-necked, round-bottomed flask equipped with a reflux condenser and heating mantle. The mixture was heated to reflux and maintained at a temperature of 144° for 20 hr. The mixture was distilled to remove xylene and unchanged starting materials and to isolate the pure Diels-Alder adduct, *i.e.*, (2-(1,4,5,6,7,7-hexachlorobicyclo[2.2.1.]-5-hepten-2-yl)methoxyethoxy)ethanol (315 g., 75%), b.p. 185°/0.2 mm., n_D^{25} 1.5335.

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Synthesis of 3,5-Diphenylphenol and a Novel Complex Thereof

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In the course of a synthetic scheme it was necessary to prepare 3,5-diphenylphenol. 3,5-Diphenylphenol (III) has been prepared by dehydrogenation of 3,5-diphenyl-2-cyclohexen-1-one[1] (I), by decarboxylation of 4,6-diphenylsalicylic acid,[2] and by decarboxylation of 2,6-dicarboxy-3,5-diphenylphenol.[3] In all cases, the yields were too small to be satisfactory in a synthetic scheme. It was reported that bromination of I with bromine followed by dehydrobromination failed to give III.[1] It was felt that repeating the preparation using

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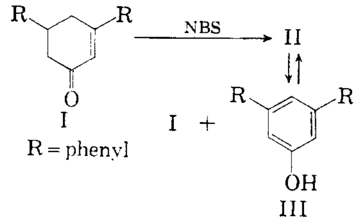
(1) A. D. Petrow, *Ber.*, **62**, 642 (1929).

(2) J. Kenner and H. Shaw, *J. Chem. Soc.*, 769 (1931).

(3) W. Deuschel, *Helv. Chim. Acta.* **34**, 168 (1951).

N-bromosuccinimide as the brominating agent might be more successful, as Deuschel reports that bromination of diethyl 2-oxo-4,6-diphenyl-6-cyclohexene-1,3-dicarboxylate with *N*-bromosuccinimide gives the corresponding phenol in excellent yield.



3,5 - Diphenyl - 2 - cyclohexen - 1 - one was prepared by the condensation of benzalacetophenone and acetoacetic ester, followed by hydrolysis and decarboxylation.[4] Bromination was readily effected with *N*-bromosuccinimide and the bromo-3,5-diphenyl-2-cyclohexen-1-one lost hydrogen bromide spontaneously. Recrystallization of the product gave 85–90% yields of a compound (II), m.p. 123–124°. The infrared spectrum indicated bonded hydroxyl (3300 cm.$^{-1}$) and conjugated carbonyl (1645 cm.$^{-1}$). The compound gave analysis corresponding to $C_{36}H_{30}O_2$.

Compound II proved to be an equimolar complex of 3,5-diphenylphenol (m.p. 94°[3]) and 3,5-diphenyl-2-cyclohexen-1-one (m.p. 82,[1] 89°[5]), and was also prepared by recrystallizing a mixture of I and III from hexane or ethanol. Compound formation was demonstrated by the method of Kofler[6] using a hot stage microscope. By heating a slide covered half by the phenol and half by the ketone, melting was observed at 85° and 92° corresponding to the two eutectics, at 89° and 94° for the two pure components, and at 124° for the compound, II.

The solution characteristics of II indicate essentially complete dissociation in dilute solution. The molecular weight, by cryoscopic or ebullioscopic methods, is 246 (theor. 246). The ultraviolet spectrum of II, in ethanol, is equal to the sum of the spectra of its two components. The strongly bonded hydroxyl frequency shifts to shorter wave lengths on dilution in chloroform as would be expected if dissociation occurred. Compound II may be separated into its components by extraction of the phenol from a solution of II in benzene-petroleum ether with Claisen's alkali or by chromatography on Woelm acid alumina grade one. The components may also be separated by the preparation of ketone (2,4-dinitrophenylhydrazone) or hydroxyl (methyl ether) derivatives. The overall yield of the phenol, using the alkali separation, based on I is 75–80%, allowing for recovered ketone. The recovered starting material from the complex may be recycled without further purification.

Apparently the spontaneous dehydrobromination begins when the bromination approaches 40–50% completion and the evolved hydrogen bromide halts further bromination. To circumvent this problem and increase the yield of III, large excesses of *N*-bromosuccinimide and peroxide catalyst were used. In these cases, the overall yield of II was reduced from 90% to 70–80% and some excess phenol was produced.

EXPERIMENTAL

3,5-Diphenyl-2-cyclohexen-1-one (I). Ethyl 4,6-diphenyl-2-oxo-3-cyclohexenecarboxylate[4] (9.0 g.) was dissolved in 50 ml. methanol and 50 ml. 10% aqueous sodium hydroxide was added. The solution was refluxed for 2 hr., cooled, and acidified with hydrochloric acid. Carbon dioxide was vigorously evolved. The solution was refluxed for 2 hr. and then concentrated. White crystals separated and were collected and dried. The product was recrystallized from ethanol giving 5.2 g. of I (85%) m.p. 82°.

Compound of 3,5-diphenylphenol and 3,5-diphenyl-2-cyclohexen-1-one (II). 3,5-Diphenyl-2-cyclohexen-1-one (2.0 g.) was dissolved in 25 ml. dry carbon tetrachloride by warming. To the solution was added 1.42 g. *N*-bromosuccinimide. The mixture was refluxed for 3 hr., during which time a red color developed. At the end of this time the reaction turned pale yellow and hydrogen bromide was evolved. After 1 hr additional refluxing the mixture was cooled and filtered to remove the succinimide. The carbon tetrachloride solution was then evaporated to dryness, leaving 2.0 g. reddish crystals, m.p. 95–98°. The product was recrystallized from hexane giving 1.75 g. (87% of theor.) of white crystals m.p. 123–124°.

A small sample recrystallized several times for analysis melted at 123.5–124.5°.

Anal. Calcd. for $C_{36}H_{30}O_2$: C, 87.42; H, 6.11. Found: C, 87.46; H, 6.16.

3,5-Diphenylphenol (III). Compound II (300 mg.) was dissolved in a mixture of 10 ml. benzene and 20 ml. petroleum ether. The solution was extracted with three 10-ml. portions of Claisen's alkali. The extract was diluted with an equal volume of water and acidified with hydrochloric acid. A tan oil separated which solidified on standing. The solid was collected and recrystallized from hexane (135 mg., m.p. 93–94°). Evaporation of the benzene-petroleum ether solution to dryness gave 150 mg. of a tan oil which crystallized from hexane giving 130 mg. I, m.p. 82–83°.

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[4] E. Knoevenagel, *Ann.*, **281**, 59 (1894).

[5] W. Dieckmann, and K. von Fischer, *Ber.*, **44**, 971 (1911).

[6] A. Kofler, *Z. physik. Chem.*, A 187, 201 (1940); A. Kofler, *Z. physik. Chem.*, 363 (1940).

Preparation of Certain 4-Acylphenols[1]

Robert A. Bragole and Robert A. Shepard

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A number of 4-acylphenols have been synthesized in conjunction with a study of ionization constants:

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[1] From the M. S. thesis research of R. A. Bragole.