

acid hydrochloride V and thionyl chloride with triethylamine in benzene under high dilution.

EXPERIMENTAL

*Methyl 15-bromopentadecanoate.*⁵ Wet silver oxide was added to molten methyl hydrogen 1,16-hexadecanedioate. The silver salt obtained was dried and dispersed in 200 ml. of dry carbon tetrachloride. To the dispersion bromine (82.5 g.) was added gradually while stirring at 40° and the stirring was continued for 2 more hr. at the same temperature. The reaction mixture was filtered, the filtrate was washed with aqueous potassium carbonate and dried with calcium chloride. The solvent was removed and the residue was distilled under reduced pressure to give faint brownish crystals, yield 55 g., b.p. 180°/0.3 mm., m.p. 36–38°.

N-Methyl-15-methylaminopentadecanamide. Thirty-three g. of methyl 15-bromopentadecanoate was dissolved in 100 g. of 30% methylamine solution in methanol and the solution was allowed to stand for 5 days at 30°. After the methanol and excess methylamine were removed, the residue was dissolved in ether. The ethereal solution was washed with aqueous potassium carbonate. The solvent was removed and the residue was distilled under reduced pressure to yield 18 g. of white crystals, b.p. 194–198°/0.05 mm., m.p. 78–79°.

Anal. Calcd. for C₁₇H₃₅ON₂: N, 9.85. Found: N, 9.62.

15-Methylaminopentadecanoic acid. *N*-methyl-15-methylaminopentadecanamide (18 g.) was dissolved in a mixture of potassium hydroxide (15 g.), water (20 ml.), and methanol (80 ml.), and heated for 40 hr. under reflux. After the methanol was removed, the residual alkaline solution was poured into 500 ml. of hot water and the pH of the solution was adjusted to 8.0 with 1*N* hydrochloric acid. The resulting precipitate weighed 8.3 g. and melted at 132–135°. Recrystallization from 50% ethanol solution gave white leaflets, m.p. 142.5–143.5°.

Anal. Calcd. for C₁₆H₃₃O₂N: N, 5.16. Found: N, 5.08.

15-Methylaminopentadecanoic acid hydrochloride. 15-Methylaminopentadecanoic acid was dissolved in hydrochloric acid and excess hydrochloric acid was removed under reduced pressure. Recrystallization of the residue from 90% acetone solution gave white leaflets, m.p. 127–128°.

Anal. Calcd. for C₁₆H₃₄O₂NCl: Cl, 11.52. Found: Cl, 11.55.

2-Methyl-2-azacyclohexadecanone. 15-Methylaminopentadecanoic acid hydrochloride (4.4 g.) was dissolved in 20 ml. of thionyl chloride. The excess thionyl chloride was removed under reduced pressure and the residue was dissolved in 50 ml. of absolute tetrahydrofuran. The solution was added to a mixture of triethylamine (35 g.) and dry benzene (3000 ml.) and then stirred at 75° for 15 hr. The reaction mixture was concentrated to about 1000 ml., washed with aqueous potassium carbonate, and the solvent was removed under reduced pressure. The residue was extracted with *n*-hexane, the extract was washed with aqueous sodium hydroxide, and the solvent was distilled. Distillation of the residue gave a clear colorless oil, 1.3 g., b.p. 150–168°/2 mm. Redistilled sample for analysis gave the following values: b.p. 172°/2.5 mm., n_D^{20} 1.4895, d_4^{20} 0.9782.

Anal. Calcd. for C₁₆H₃₁ON: N, 5.53. Found: N, 5.49.

Molecular weight. Calcd. for C₁₆H₃₁ON: 253. Found: 251.

Molecular refraction. Calcd. for C₁₆H₃₁ON: 77.759. Found: 77.234.

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(5) P. Chiut and J. Hausser, *Helv. Chim. Acta*, **12**, 463 (1929).

Diels-Alder Adducts of Hexachlorocyclopentadiene with Allyloxyalkanols

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Many Diels-Alder adducts of hexachlorocyclopentadiene have been reported^{1,2} with most classes of dienophiles. Of these adducts there have been a number with reported biological activity. In the field of agricultural chemistry one of the pressing weed control problems is that of aquatic plant life; the destruction of bothersome aquatic plants is particularly important in drainage and other service ditches. Hexachlorocyclopentadiene itself has shown some activity as an aquatic herbicide³; it has, however, the disadvantages of low water solubility and relatively high toxicity. Simple Diels-Alder adducts of hexachlorocyclopentadiene have been prepared from olefins possessing water solubilizing groups and these have as a rule been less toxic than the parent diene. For example, adducts have been prepared from allyl glycidyl ether⁴ and from divinyl ether⁵; sulfite derivatives have been prepared from the adduct with 2-butyne-1,4-diol.⁶ As a rule these have biological activity and possess greater water solubility than hexachlorocyclopentadiene itself.

This report describes the preparation of a series of adducts of hexachlorocyclopentadiene with dienophiles which might display enhanced water compatibility while at the same time retaining herbicidal activity. A series of allyloxy derivatives was prepared from allyl alcohol with ethylene oxide, 1-butylene oxide, and styrene oxide. These compounds (see Table I) were utilized in a standard preparative procedure with hexachlorocyclopentadiene to obtain the Diels-Alder adducts (see Table II). Purified samples of the compounds were tested against the several organisms. It is interesting that the adducts from 2-allyloxyethanol, 2-(allyloxyethoxy)ethanol, and 1-allyloxy-2-butanol were reasonably soluble or emulsifiable in water whereas the adduct from 2-allyloxy-1-phenylethanol was only slightly soluble; the biological activity of the first three adducts against both water weeds and other test organisms is of interest. The 2-allyloxyethanol and 2-(allyloxyethoxy)ethanol adducts both show pronounced activity as insecticides and herbicides as well as inhibition in micro-

(1) C. W. Roberts, *Chem. & Ind. (London)*, 110 (1958).

(2) H. E. Ungnade and E. T. McBee, *Chem. Revs.*, **58**, 249 (1958).

(3) Personal communication, Dr. K. Leasure, The Dow Chemical Company.

(4) W. L. Bressler and J. C. Smith, U. S. Patent, **2,834,790** (May 13, 1958).

(5) A. Goldman, U. S. Patent **2,795,619** (June 11, 1957).

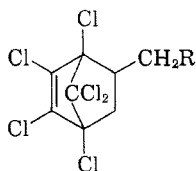
(6) British Patent **810,602** (March 18, 1959).

TABLE I
ALLYLOXYALKANOLS
 $\text{CH}_2=\text{CHCH}_2\text{OR}$

Substituent R	B.P.°	mm.	n_D^{25}	Literature Values		
				B.P.°	mm.	n_D
$\text{CH}_2\text{CH}_2\text{OH}$	56	10	1.4326	159-160	atm	1.4355(20) ^a
				58-60	20	1.4360(20) ^b
$(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$	106	10	1.4445	98-101	2	1.4440(20) ^a
$\text{CH}_2\text{CHOHC}_2\text{H}_5$	95	60	1.4312
$\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{OH}$	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. Kotreev and I. K. Rubstova, *Khim Prom.*, **1953**, 8; *Chem. Abstr.*, **50**, 6384 (1956). ^c Anal. Calcd. for $\text{C}_7\text{H}_{14}\text{O}_2$: 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		Hydrogen		Chlorine	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
$\text{OCH}_2\text{CH}_2\text{OH}$	72	167	0.3	1.5446	32.03	31.75	2.69	2.51	56.74	57.40
$\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$	75	185	0.2	1.5335	34.40	34.29	3.37	3.43	50.78	50.55
$\text{OCH}_2\text{CHOHC}_2\text{H}_5$	62	164	0.2	1.5319	35.76	36.21	3.50	3.49	52.79	52.80
$\text{OCH}_2\text{CH}(\text{C}_6\text{H}_5)\text{OH}$	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-one¹ (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

- (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).