enous pressure at 190–205° for 2 hr. After cooling, water and ether/acetone were added to dissolve all the solids. The ethereal layer was separated, washed with water, dried over sodium sulfate, and diluted with methanol. Partial evaporation of this solution gave white needles (5 g., 79%) of octachloroindene, which were found to be very sensitive to light. The analytical sample, prepared by repeated crystallization from methanol, melted at 138–138.5°, $\lambda_{\rm max}^{\rm KB}$ 6.29 μ , $\lambda_{\rm max}^{\rm CHBOH}$ (ϵ), 236 m μ (19,500), 242 m μ (21,000), 250 m μ (29,000), 259 m μ (31,000).

Anal. Caled. for C₉Cl₈: C, 27.59; Cl, 72.41. Found: C, 27.52; Cl, 72.23.

Chlorination of V; decachloroindane (VI). Chlorine gas was bubbled through a solution of 5 g. of V in 75 ml. of carbon tetrachloride held at 50° for 2 hr. Evaporation of the solvent and crystallization of the residue from methanol gave 4.8 g. (81%) of white crystalline material, m.p. 134-135°, identical with a sample of decachloroindane (VI) prepared by the destructive chlorination of naphthalene as described by Vollmann.¹⁴

Anal. Caled. for C₉Cl₁₀: Cl, 76.64. Found: Cl, 76.51.

Hydrolysis of V; hexachloroindone (IV). Five grams of V were dissolved in 25 ml. of liquid sulfur trioxide. The excess sulfur trioxide was allowed to evaporate overnight from an open beaker. The remaining sulfuric acid-solid mixture was washed with cold water, and the solid crystallized from methanol to give a nearly quantitative yield (4.4 g.) of IV, m.p. 149-150°.

Hexachloroindane-1,3-dione (VII). Five grams of VI were treated with liquid sulfur trioxide in the same manner as above. A quantitative yield (3.8 g.) of VII was obtained as bright yellow crystals, m.p. 155-156°, λ_{max}^{ccl} 5.65, 5.75 μ .

Anal. Calcd. for C₂Cl₆O₂: Cl, 60.30. Found: Cl, 60.28.

This material was identical with a sample prepared by treatment of VI with anhydrous nitric acid as described by Bernimolin.¹⁵

Oxidation of VII. Three grams of potassium permanganate in 50 ml. of aqueous 5% sodium hydroxide was added with stirring to 1 g. of VII in 10 ml. of warm acctone. After 4 hr., the solution was acidified with concd. hydrochloric acid, bleached with sulfur dioxide, saturated with ammonium sulfate, and extracted with ether. The ethereal extract was washed with water and evaporated to dryness. Sublimation of the residue gave crystals of tetrachlorophthalic anhydride, m.p. 254-256°, identical with an authentic sample.

Acknowledgment. The authors are indebted to Dr. Everett E. Gilbert for his advice and counsel.

DEPARTMENT OF CHEMISTRY HARVARD UNIVERSITY CAMBRIDGE, MASS.

GENERAL CHEMICAL DIVISION Allied Chemical Corp. Morristown, N. J.

Macrocyclic Compounds. 2-Methyl-2-azacyclohexadecanone

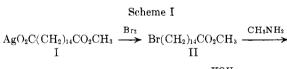
YOSHIO IWAKURA AND KEIKICHI UNO

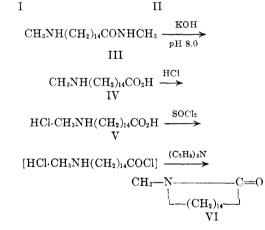
Received October 1, 1959

Since the structure of natural musk was established as that of a macrocyclic ketone,¹ many macrocyclic compounds have been synthesized. An assumption that cyclic compounds with an approximately 15-membered ring give a musklike odor independent of the type of atoms in the ring skeleton was presented by Ruzicka *et al.*² However, in the syntheses of macrocyclic ureas³ and macrocyclic amides,⁴ we found that they gave no odor. Because of the big intermolecular attraction possibly by H-bonding of the compounds which contain urea- or amide-linkages, it is understood that the melting point becomes high and the volatility becomes low. Assuming that the absence of

odor in the macrocyclic ureas and macrocyclic amides was due to their strong intermolecular attraction, we carried out the syntheses of macrocyclic N-alkyl amides and N,N'-dialkyl ureas in which there is no possibility of H-bonding. 2-Methyl-2-azacyclohexadecanone was synthesized from 1,16-hexadecanedioic acid and was found to have a musklike odor.

The sequence of reactions used is shown in Scheme I. In the reaction of the bromoester (II) with methylamine, N-methyl-15-methylaminopentadecanamide (III) rather than methyl 15methylaminopentadecanoate was obtained. 15-Methylaminopentadecanoic acid (IV) was obtained by hydrolysis of III with alcoholic potassium hydroxide, followed by adjusting the pHof the solution to 8.0.





When the hydrochloride (V) of the amino acid was treated with thionyl chloride, the amino acid chloride hydrochloride was apparently formed. 2-Methyl-2-azacyclohexadecanone (VI) was prepared by treating the reaction product of amino

⁽¹⁾ L. Ruzicka, Helv. Chim. Acta, 9, 715, 1008 (1926).

⁽²⁾ L. Ruzicka, G. Salomon, and K. E. Meyer, *Helv. Chim.* Acta, 17, 882 (1934).

⁽³⁾ Y. Iwakura, K. Uno, and M. Nakada, J. Chem. Soc. Japan, 80, 78 (1959).

⁽⁴⁾ Presented at the 12th meeting of the Chemical Society of Japan, Kyoto, April 1959.

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 C17H36ON2: 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 1N 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 $C_{16}H_{32}O_2N$: N. 5.16. Found: N. 508. 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. Caled. for $C_{16}H_{34}O_2NCl$: 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_{20}^{*0} 1.4895, d_{4}^{*0} 0.9782.

Anal. Caled. for $C_{16}H_{s1}ON$: N, 5.53. Found: N, 5.49. Molecular weight. Caled. for $C_{16}H_{s1}ON$: 253. Found:

251. Molecular refraction. Calcd. for $C_{16}H_{a1}ON$: 77.759. Found: 77.234.

RESEARCH LABORATORY OF RESOURCES UTILIZATION Tokyo Institute of Technology Meguroku, Tokyo, Japan

Diels-Alder Adducts of Hexachlorocyclopentadiene with Allyloxyalkanols

CARLETON W. ROBERTS AND DANIEL H. HAIGH

Received February 2, 1960

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-

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

⁽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).