1,4-Bis(allyloxy)-2,3,5,6-tetrachlorobenzene (II). Tetrachlorohydroquinone (62.0 grams; 0.25 mole) was dissolved in absolute methanol (270 ml.) contained in a 1-liter, round-bottomed flask equipped with a reflux condenser, pressure equalizing addition funnel, thermometer, and a mechanical stirrer.

To the vigorously stirred solution maintained at 30° C. under a nitrogen atmosphere was added dropwise over a 10-minute period a solution of sodium methoxide (14.5 grams assaying 95%; 0.255 mole) dissolved in methanol (105 ml.). Allyl chloride (23.0 grams; 0.3 mole) was added during 15 minutes, while the temperature was maintained at 30° to 35° C. After being refluxed for 20 hours, the reaction mixture was cooled to 30° C. and treated with a second portion of sodium methoxide (14.5 grams; 0.255 mole), followed by addition of allyl chloride (23.0 grams; 0.3 mole) in a manner similar to that described above. The reaction mixture, a brown-colored suspension, was cooled to +5° C. and filtered. The crystalline precipitate was stirred with two portions of 250 ml. of water and once with 250 ml. of 0.4% aqueous solution of sodium hydroxide. The crystals were washed with 250 ml. of water and sucked dry. Drying under reduced pressure at 50° to 60° C. gave 49.2 grams (60% yield) of 1,4-bis(allyloxy)-2,3,5,6-tetrachlorobenzene (diallyl ether of tetrachlorohydroquinone), m.p. 124°–125° C. After crystallization from methanol, the compound melted at 126.6°–127.5° C. Anal. Calcd. for $C_{12}H_{10}Cl_4O_2$: C, 43.95; H, 3.05; Cl, 43.25. Found: C, 44.11; H, 3.39; Cl, 42.70. The infrared spectrum showed absorption maxima at 3091 cm.$^{-1}$ (m), 3022 cm.$^{-1}$ (m), 2989 cm.$^{-1}$ (m), 2950 cm.$^{-1}$ (m), 2895 cm.$^{-1}$ (m),1885 cm.$^{-1}$ (w), 1644 cm.$^{-1}$ (w), 1468 cm.$^{-1}$ (w), 1433 cm.$^{-1}$ (m), 1408 cm.$^{-1}$ (vs), 1370 cm.$^{-1}$ (s), 1330 cm.$^{-1}$ (m, shoulder), 1285 cm.$^{-1}$ (m), 1238 cm.$^{-1}$ (w), 1222 cm.$^{-1}$ (w), 1168 cm.$^{-1}$ (m),1153 cm.$^{-1}$ (w), 992 cm.$^{-1}$ (s), 980 cm.$^{-1}$ (vs), 963 cm.$^{-1}$ (vs), 936 cm.$^{-1}$ (s), 865 cm.$^{-1}$ (s), 714 cm.$^{-1}$ (s) and 689 cm.$^{-1}$ (m).

1,4 - Bis(2,3 - dibromopropoxy) - 2,3,5,6 - tetrachlorobenzene (III). 1,4-Bis(allyloxy)-2,3,5,6-tetrachlorobenzene (32.8 grams; 0.1 mole) was dissolved in boiling carbon tetrachloride (130 ml.) contained in a 300-ml., round-bottomed flask equipped with a thermometer, an addition funnel, a mechanical stirrer, and a reflux condenser. To the vigorously stirred solution was added over a 25-minute period a solution of bromine (32.6 grams; 0.204 mole) in carbon tetrachloride, while the temperature was maintained at 78°–80° C. After the addition was completed, stirring was continued for 15 minutes. Filtration and crystallization of the precipitate from carbon tetrachloride gave 52.8 grams (81.5% yield) of 1,4-bis(2,3-dibromopropoxy)-2,3,5,6-tetrachlorobenzene, m.p. 172.0°–172.8° C. Anal. Calcd. for $C_{12}H_{10}Br_4Cl_4O_2$: C, 22.30; H, 1.55; Cl, 21.90; Br, 49.30. Found: C, 22.11; H, 1.70; Cl, 21.55; Br, 48.84. The infrared spectrum showed absorption maxima at 2925 cm.$^{-1}$ (m), 2855 cm.$^{-1}$ (m), 1930 cm.$^{-1}$ (w), 1690 cm.$^{-1}$ (m, shoulder), 1645 cm.$^{-1}$ (s), 1630 cm.$^{-1}$ (s, shoulder), 1588 cm.$^{-1}$ (m), 1455 cm.$^{-1}$ (m), 1395 cm.$^{-1}$ (m), 1285 cm.$^{-1}$ (s), 1252 cm.$^{-1}$ (s), 1143 cm.$^{-1}$ (s), 1115 cm.$^{-1}$ (s), 1098 cm.$^{-1}$ (m), 1048 cm.$^{-1}$ (m), 1029 cm.$^{-1}$ (m), 1020 cm.$^{-1}$ (m), 992 cm.$^{-1}$ (m, shoulder), 967 cm.$^{-1}$ (m), 948 cm.$^{-1}$ (m, shoulder), 833 cm.$^{-1}$ (m), 771 cm.$^{-1}$ (w), 743 cm.$^{-1}$ (m), 688 cm.$^{-1}$ (m), 670 cm.$^{-1}$ (m), 651 cm.$^{-1}$ (w), 620 cm.$^{-1}$ (w), and 590 cm.$^{-1}$ (w).

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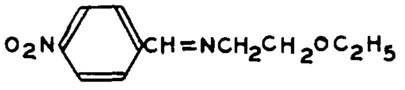
Azomethine Derivatives of β-Ethoxyethylamine

ALEKSEY A. SIROTENKO and C. PETER COLE
Department of Chemistry, St. John Fisher College, Rochester, N. Y.

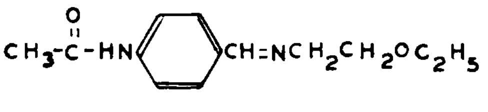
Syntheses of *N*-(*p*-nitrobenzylidene)-β-ethoxyethylamine and *N*-(*p*-acetamidobenzylidene)-β-ethoxyethylamine are described.

THE use of β-ethoxyethylamine as an unknown compound in a qualitative organic analysis course requires the existence of known, suitable derivatives. Heilbron (*3*) mentions picrate and picrolonate derivatives only. The literature describes derivatives produced by the reaction of β-ethoxyethylamine with 1,3-bis(*N*-acetylsulfanilyl)urea (*1*), *N,N'*-bis(acetylsulfanilyl)urea, and *N*-(ethoxyethyl)-*N'*-(acetylsulfanilyl)urea (*2*). β-Ethoxyethylamine condenses with *p*-nitrobenzaldehyde and *p*-acetamidobenzaldehyde to give typical azomethines (I and II respectively).

The preparation and purification of these derivatives are easy and the yields are excellent.



I



II

EXPERIMENTAL

Condensation with p-Nitrobenzaldehyde. A mixture of *p*-nitrobenzaldehyde (3.022 grams, 0.02 mole), methanol (25 ml.) and β-ethoxyethylamine (2.228 grams, 0.025 mole) was refluxed for 30 minutes and the resulting yellow solution cooled in the refrigerator for 1 hour. The precipitate was filtered and washed three times with 25-ml. portions of distilled water. The slightly cream-colored needles were air-dried, then dried over $CaCl_2$ for 24 hours in a desiccator. The yield was 4.1 grams (84.5%) (m.p. 55.0-55.5° C.). Recrystallization gave the same melting point.

Analysis. Calculated for $C_{11}H_{14}N_2O_3$: C, 59.45; H, 6.35; N, 12.60. Found: C, 59.27; H, 6.42; N, 12.52.

Condensation with p-Acetamidobenzaldehyde. A mixture of *p*-acetamidobenzaldehyde (3.259 grams, 0.02 mole), methanol (25 ml.), and β-ethoxyethylamine (1.780 grams, 0.02 mole) was refluxed 30 minutes and the methanol evaporated on the water bath. The resulting oily residue or yellow solid which formed on cooling was dissolved in 5 ml. of ethyl acetate with warming on the water bath and stirring to effect dissolution. Cyclohexane (50 ml.) was then added with stirring and the resulting precipitate was filtered and washed with 20 ml. of cyclohexane. The cream-colored, very fine needles were then air-dried. The yield was 3.2 grams (63.51%) (m.p. 93-94° C.). Repeated purification with cyclohexane gave the same melting point.

Analysis. Calculated for $C_{16}H_{21}N_3O_2$: C, 66.87; H, 7.37; N, 14.62. Found: C, 66.71; H, 7.40; N, 14.55.

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Synthesis and Thermal Decomposition of Tetrasubstituted Ureas

C. C. CHAPPELOW, Jr., R. N. CLARK, and F. V. MORRISS
Midwest Research Institute, Kansas City, Mo.

A number of new tetraalkylureas, aryltrialkylureas, dialkyldiarylureas, alkyltriarylureas, and tetraarylureas were prepared and characterized. Several new acetamides, amines, and disubstituted carbamoyl chlorides were synthesized as intermediate compounds for the urea syntheses. A study of the thermal decompositiion of several tetraalkylureas indicated that the first step of degradation involves a β-elimination reaction.

A STUDY of the synthesis and thermal decomposition of a variety of tetrasubstituted ureas was conducted as part of a program dealing with the development of new synthetic lubricants.

EXPERIMENTAL

Synthetic Methods. TETRASUBSTITUTED UREAS (Table I). *Method A. Preparation of Tetra-n-decylurea* (Compound V, Table I). Di-*n*-decylamine (42.8 grams, 0.48 mole) and 500 ml. of toluene were placed in a 1-liter flask equipped with thermometer, stirrer, reflux condenser, and gas inlet tube. Phosgene (23.8 grams, 0.24 mole) was bubbled into the stirred reaction mixture while the temperature was held below 35° C. by applying external cooling. After the addition was complete, the reaction mixture was slowly heated to 110° C. and held there for 16 hours with stirring. The toluene was distilled off and the residue refluxed and stirred with 200 ml. of KOH solution for 1.5 hours. This reaction mixture was extracted with 300 ml. of ether. The ether layer was separated and dried over anhydrous Na_2SO_4, and the ether was stripped off, leaving a crude residual liquid. Purified product was obtained after two distillations. It was