acetonitrile and cuprous chloride by extraction with hot benzene, from which it crystallized on cooling.

Anal. Calcd. for $C_{13}H_{11}ClNCu$: C, 57.53; H, 3.79. Found: C, 57.34; H, 3.48.

Evaporation of the cooled benzene extracts afforded a 40–50% yield of II, admixed with the unidentified compound described below. If the original reaction mixture was distilled before extraction with benzene, there remained in the undistilled residue an organic compound of high melting point which contained nitrogen. In a run using the same amounts of starting materials as described for benzhydryl bromide, about 4–5 g. of this benzene-soluble compound was formed. Its identification was not undertaken.

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Synthesis of Diphenylalkylcyclopentanones

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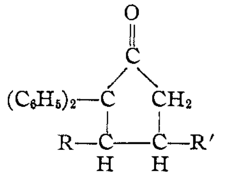
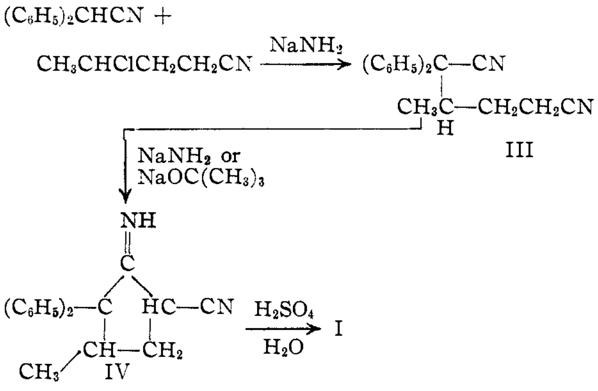
No preparation of diphenylalkylcyclopentanones has been reported in the literature and due to their similarity to a deaminated, cyclized Methadone it seemed advisable to investigate the synthesis of compounds of this type.



I, R' = H
R = CH_3
II, R' = CH_3
R = H

Two examples—2,2-diphenyl-3-methylcyclopentanone (I) and 2,2-diphenyl-4-methylcyclopentanone (II) were selected. The synthesis of I is shown in the following scheme.



Reaction of 1-iodo-3-chlorobutane with one mole of sodium cyanide converted this compound to γ-chlorovaleronitrile, which was condensed with diphenylacetonitrile in the presence of sodamide to give III. However, considerable cyclization to IV occurred during this reaction. The linear compound III could then be cyclized with sodamide or in a better yield using sodium tertiary butoxide as the catalyst. The hydrolysis and decarboxylation of IV gave I.

The ketone II was prepared in a similar manner using γ-chloroisovaleronitrile.

γ-Chloroisovaleronitrile (V) was prepared from γ-chloroisobutyl bromide by treatment with an equivalent of sodium cyanide.

Experimental

The 1,3-dichlorobutane was prepared according to Clarke and Streight.[1] The 1-iodo-3-chlorobutane was prepared according to Hass and Huffman.[2]

Preparation of γ-Chlorovaleronitrile.—Into a three-neck one-liter flask equipped with a dropping funnel, a mechanical stirrer, and a gas trapped reflux condenser was placed 10.1 g. (0.206 mole) of sodium cyanide and 60 cc. of water. After solution of the sodium cyanide 200 cc. of 95% ethyl alcohol was added, followed by 37.5 g. (0.172 mole) of 1-iodo-3-chlorobutane. The mixture was refluxed for six hours and then cooled. The cooled solution was diluted with 225 cc. of water and the solution was then extracted with three 50-cc. portions of chloroform. The chloroform layers were separated and washed twice with an equal volume of half-saturated calcium chloride solution, and then washed twice with an equal volume of water. The organic layer was dried over calcium chloride and stored in the refrigerator in a container covered with aluminum foil to prevent decomposition. The solution was filtered and the filtrate subjected to a distillation to remove the chloroform. The residue was then distilled under reduced pressure and 14.6 g. (72.3% yield) of a clear colorless liquid with a boiling range of 95–110° at 40–44 mm. pressure was collected. Gresham[3] found the boiling point to be 55° at 2 mm.

Condensation of γ-Chlorovaleronitrile and Diphenylacetonitrile in the Presence of Sodamide.—Into a three-neck 500-cc. flask equipped with a dropping funnel, a mechanical stirrer, and a reflux condenser with attached calcium chloride drying tube was placed 250 cc. of dry benzene followed by 5.3 g. (0.136 mole) of sodamide. To this mixture was added with stirring, 25 g. (0.129 mole) of diphenylacetonitrile. The mixture was refluxed for three hours, during which time evolution of ammonia occurred (during this period the drying tube was removed for the condenser), and then cooled to room temperature. To the resulting mixture was added dropwise 14.6 g. (0.124 mole) of γ-chlorovaleronitrile. The mixture was refluxed for four hours, cooled and then poured into 300 cc. of water. The layers were separated, the benzene layer washed three times with an equal volume of water and then dried over anhydrous magnesium sulfate. After filtration of the magnesium sulfate, the benzene was removed from the solution by distillation. The resulting oil was placed in the refrigerator. Within 48 hours, partial crystallization had occurred. The oil was filtered and the crystalline solid was carefully washed with ether. Approximately 1.5 g. of a solid was obtained which, when recrystallized from methanol, yielded white crystals melting at 164–166°.

The balance of the oil and the ethereal washings when concentrated and then subjected to a series of fractional distillations at one mm. pressure, yielded 8.5 g. of diphenylacetonitrile from the fraction distilling at 0–150° and 1.5 g. of the cyclic ketimine from the fraction distilling at 150–210°. The total yield of 2,2-diphenyl-3-methyl-5-cyanocyclopentanone imine was 3 g. (8.8% yield).

Anal. Calcd. for $C_{19}H_{18}N_2$: N, 10.22. Found: N, 10.10.

Preparation of 2,2-Diphenyl-3-methylcyclopentanone.—Into a one-neck 200-cc. flask equipped with a reflux condenser was placed 1.4 g. (0.00511 mole) of finely divided 2,2-diphenyl-3-methyl-5-cyanocyclopentanone imine and a cold sulfuric acid solution made up of 1.5 cc. of water and 5 cc. of concentrated sulfuric acid. After the addition was complete, the flask was heated on a water-bath until solution occurred and then for 15 minutes longer. The solution was cooled and 25 cc. of water added. The mixture was then heated to reflux, at which time 30 cc. of glacial acetic acid was added to increase the miscibility of the two layers present, and the solution was refluxed for 25 hours. The reaction mixture was then cooled, diluted with 200 cc. of water, and extracted with three 40-cc. portions of ether. The ether layers were combined and washed with several portions of 5% sodium hydroxide solution, and dried over anhydrous magnesium sulfate. The solution was filtered and the filtrate concentrated under reduced pressure until the volume was reduced to 5–8 cc. (at this point some nearly white solid had formed) and was then stored in the

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[1] R. H. Clarke and H. R. L. Streight, *Trans. Roy. Soc. Can. Series* 3, Vol. 23, Sec. III (77) 1929.

[2] H. B. Hass and H. C. Huffman, THIS JOURNAL, **63**, 1233 (1941).

[3] Wm. F. Gresham, U. S. Patent 2,405,948.

refrigerator. Within 24 hours a crystalline mass had formed in the flask. The supernatant liquid was decanted and the solid was recrystallized from methanol. The one gram of product (78.3 yield) was then sublimed at one mm. pressure for further purification, and this procedure gave a white crystalline product melting at 92.5–94°.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.20; H, 7.26.

Preparation of γ-Chloroisovaleronitrile.—γ-Chloroisobutyl bromide was prepared according to Hearne, *et al.*[4]

Into a three-neck three-liter flask equipped with a gas-trapped reflux condenser, a mechanical stirrer, and a dropping funnel were placed 100 ml. of water and 103 g. (2 moles) of sodium cyanide. After solution of the cyanide, 700 ml. of 95% ethyl alcohol was added, followed by 305 g. (1.78 moles) of γ-chloroisobutyl bromide. The mixture was refluxed for two hours, cooled, and 600 ml. of water was added, followed by 200 ml. of chloroform. The layers were separated, and the chloroform layer was washed with an equal volume of water. After drying over calcium chloride, the chloroform was removed from the solution at atmospheric pressure, and the residue was fractionated at 15 mm. pressure. The fraction boiling at 79–83° and weighing 58 g. (27.7% yield) was collected. Cloke, *et al.*,[5] found the boiling point to be 82–83° at 16 mm.

Condensation of γ-Chloroisovaleronitrile with Diphenylacetonitrile.—The sodium salt of 19.3 g. (0.1 mole) of diphenylacetonitrile was prepared by refluxing 4.3 g. (0.11 mole) of sodamide with diphenylacetonitrile in 300 ml. of dry benzene for 90 minutes. The mixture was cooled, and 22 g. (0.2 mole) of γ-chloroisovaleronitrile was added dropwise with stirring. The resulting mixture was refluxed for 12 hours, cooled and poured into an equal volume of water. The organic layer was separated, washed with water and dried over anhydrous magnesium sulfate. After removal of benzene under vacuum, the mixture was distilled until the vapor temperature reached 80° at 15 mm. Distillation at 2 mm. pressure gave as a first fraction diphenylacetonitrile, secondly an oil which was a mixture of diphenylacetonitrile and the product VI and a third fraction which was VII. The second fraction was cyclized as shown below.

Cyclization to 2,2-Diphenyl-4-methyl-5-cyanocyclopentanone Imine.—Into a three-neck 200-ml. flask equipped with a mechanical stirrer and a reflux condenser was placed 50 ml. of dry *t*-butyl alcohol and 0.2 g. of sodium metal. The mixture was refluxed until complete solution of the sodium occurred, and 8 g. of the second fraction from the preceding reaction, dissolved in 20 ml. of dry *t*-butyl alcohol, was added all at once. The mixture was refluxed for four hours, cooled and one ml. of water was added. The solution was evaporated to 50 ml., whereupon trituration with petroleum ether caused crystallization. After two recrystallizations from methanol, white crystals of 2,2-diphenyl-4-methyl-5-cyanocyclopentanone imine, melting at 133–135°, were obtained.

Anal. Calcd. for $C_{19}H_{18}N_2$: N, 10.22. Found: N, 10.12.

Preparation of 4-Methyl-2,2-diphenylcyclopentanone from the Iminonitrile VII.—A mixture of 2.3 g. of the iminonitrile (VII) 4.5 ml. of concd. sulfuric acid and 1.3 ml. of H_2O was warmed on a steam-bath until the solid dissolved and the resulting solution was heated on the steam-bath for 20 minutes. The solution was cooled and a mixture of 20 ml. of water and 20 ml. of acetic acid was added. The resulting mixture was refluxed for 20 hours. It was then cooled and extracted with ether. The ether layer, after being washed with water and then with a solution of sodium bicarbonate, was dried over magnesium sulfate. After distillation of the solvent an oily residue remained. This was dissolved in petroleum ether and the solution was cooled with Dry Ice, the crystals which separated were recrystallized from a mixture of methanol and water and gave 1.4 g. (66.3%) of product which melted at 58.5–59.5°.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.55; H, 7.33.

The 2,4-dinitrophenylhydrazone melted at 191–192° after being recrystallized from ethyl acetate.

Anal. Calcd. for $C_{24}H_{22}N_4O_4$: N, 13.03. Found: N, 13.10.

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[4] G. Hearne, Ervin Stehr, T. R. Steadman and L. C. Westcott, *Ind. Eng. Chem.*, **33**, 385 (1941).

[5] J. B. Cloke, Ervin Stehr, T. R. Steadman and L. C. Westcott, THIS JOURNAL, **67**, 1587 (1945).

Dipole Moments and Structure of Acid Amides

BY W. D. KUMLER

In a recent paper Bates and Hobbs[1] imply that they were unable to calculate the dipole moment of acetamide from our data[2] because it scattered so widely. In Fig. 1 is a graph of the data showing that all three points fall near a straight line. The dipole moment of acetamide calculated from this line by the method of Halverstadt and Kumler[3] has a value of 3.92 *D* in good agreement with the value of 3.90 *D* reported by Bates and Hobbs.

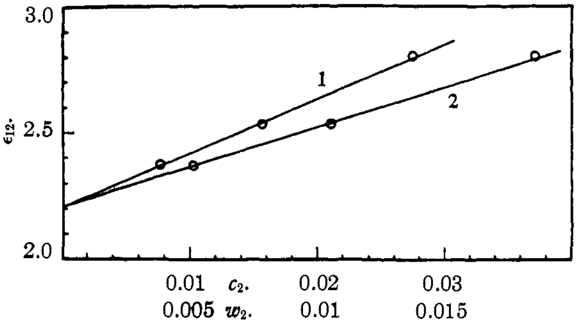

Fig. 1.—Plot of ϵ_{12} *vs.* c_2 (curve 1) for acetamide taken directly from Kumler and Porter's paper THIS JOURNAL, **56**, 2549 (1934), and a plot of ϵ_{12} *vs.* w_2 (curve 2) for the same solutions.

These authors claim the usual polar resonance form makes a negligible contribution to the structure of amides because the theoretical moment of acetamide of 3.1 *D* which they calculate from the dimensions and angles obtained in the crystalline state, is near the gas value of 3.4–3.5 *D*.[4] This argument can have validity only if the molecule has the same configuration in the gas as it has in the crystal. No evidence has been given that this is the case. If it is assumed that the molecule does have the same configuration in the gas as in the crystal, it becomes pertinent to inquire how the molecule could be so held in the gas. The structure they have assumed is coplanar with one of the N–H dipoles pointing in nearly the same direction as the C=O dipole. This structure is opposed by both dipole or electrostatic forces and steric effects, since these would cause both amino hydrogens to be as close as possible to the oxygen atom and as far as possible from the methyl hydrogens. The absence of crystal forces leaves only resonance to account for the molecule having a planar configuration in the gas. Furthermore, the resonance must be of considerable magnitude to overcome both the dipole interaction and steric effects and, hence

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[1] W. W. Bates and M. E. Hobbs, THIS JOURNAL, **73**, 2151 (1951).

[2] W. D. Kumler and C. W. Porter, *ibid.*, **56**, 2549 (1934).

[3] I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).

[4] They do not state how this gas value was obtained, but presumably it is an estimate obtained by analogy with the known gas and solution values of formamide.