stirred, with 100 g. of concentrated sulfuric acid. The mixture was cooled to 15° and quickly extracted with three 200-ml. portions of ethyl ether. The extract was dried under nitrogen over Drierite and filtered into a distilling flask. Nitrogen was bled slowly into the system while the ether was removed under reduced pressure and the mercaptopivalic acid was distilled; yield 70 g. or 53%, b.p. 101–102° (1 mm.).

Anal. Calcd. for $C_5H_{10}O_2S$: C, 44.72; H, 7.51; S, 23.90. Found: C, 44.44; H, 7.26; S, 23.47.

Dithiodipivalic Acid.—To a stirred solution of sodium hydrosulfide ($NaSH \cdot 2H_2O$, 430 g.) in water (1000 ml.), bromopivalic acid (360 g.) was added in small increments. Upon completion of the addition, more water (1000 ml.) was added and the solution was boiled for 1 hour. The solution was then transferred to the autoxidation column depicted in Fig. 1 and treated with finely dispersed air at a rate of 1000 ml. per minute for 24 hours while the temperature was maintained at 35 ± 2° by external heating when necessary. The clear solution was removed from the column and treated with 200 g. of concentrated sulfuric acid to obtain a white oil which separated and quickly solidified. This solid was collected on a filter, dried at 65°, and dissolved in ethyl alcohol. The solution was filtered to remove elemental sulfur, treated at its boiling point with two-thirds its volume of water and allowed to cool. The crystals of dithiodipivalic acid which separated were dried at 65°; yield 214 g. or 80.5%, m.p. 153–154°.

Anal. Calcd. for $C_{10}H_{18}O_4S_2$: S, 23.05; neut. equiv., 133.2. Found: S, 24.17; neut. equiv., 133.1.

Disulfoxydipivalic Acid.—Dithiodipivalic acid (25 g.) was added to a stirred solution of nitric acid (sp. gr. 1.42, 95 ml.) and water (105 ml.) and allowed to stand overnight at 35–40°. The solution was then placed on a steam-bath to bring about a vigorous reaction with formation of a white precipitate. The product was recrystallized from boiling water; yield 5.6 g. or 20%, m.p. 179–180°.

Anal. Calcd. for $C_{10}H_{18}O_6S_2$: C, 40.30; H, 6.08; S, 21.48; neut. equiv., 149.2. Found: C, 40.57; H, 6.31; S, 21.22; neut. equiv., 149.2.

Dithiodipivalyl Chloride.—Dithiodipivalic acid (50 g.) was refluxed with thionyl chloride (150 g.) for 3 hours. The excess thionyl chloride was removed at reduced pressure, and the dithiodipivalyl chloride was then distilled; yield 35.4 g. or 62%, b.p. 186–187° (7 mm.).

Anal. Calcd. for $C_{10}H_{16}Cl_2O_2S_2$: S, 21.15. Found: S, 20.90.

Diethyl Dithiodipivalate.—This compound, which has a strong onion-like odor, was obtained by the action of dithiodipivalyl chloride on ethyl alcohol; yield 91%, b.p. 178–179° (4 mm.).

Anal. Calcd. for $C_{14}H_{26}O_4S_2$: S, 19.87. Found: S, 19.61.

Dithiodipivalamide and Dithiodipivalo-*p*-toluidide.—Both of these compounds were prepared by a standard procedure.[10] The yield of amide was 82%, m.p. 164–165°.

Anal. Calcd. for $C_{10}H_{20}N_2O_2S_2$: S, 24.25; N, 10.61. Found: S, 24.01; N, 10.37.

The yield of *p*-toluidide was 76%, m.p. 136–137°.

Anal. Calcd. for $C_{24}H_{32}N_2O_2S_2$: S, 14.37; N, 6.28. Found: S, 14.21; N, 6.26.

Sulfopivalic Acid Monohydrate.—Dithiodipivalic acid (100 g.) was added in small increments to a stirred mixture of nitric acid (sp. gr. 1.42, 450 g.) and water (200 g.) at such a rate that the reaction temperature was maintained at 60–70°. The mixture was then heated on a steam-bath for 30 minutes before being allowed to evaporate in a current of air for 16 hours. The residue was distilled under reduced pressure (160 mm.) until the base temperature reached 60°. The residue was concentrated in a vacuum desiccator over sulfuric acid to obtain a slush of crystals which were removed periodically and dried over phosphorus pentoxide at a pressure of 1 mm.; yield 100 g. or 67%, m.p. 107–108°. A sample for analysis was obtained by recrystallization from a mixture of chlorobenzene and ligroin.

(10) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 158.

Anal. Calcd. for $C_5H_{12}O_6S$: S, 16.00; neut. equiv., 100. Found: S, 16.29; neut. equiv., 99.8.

Anhydrous Sulfopivalic Acid.—The acid monohydrate (10 g.) was heated at 118° for 4 hours at a pressure of 1 mm. in a drying apparatus containing phosphorus pentoxide as the desiccant. The gray powder thus produced was dissolved in hot benzene and treated with an equal volume of ligroin. Upon cooling the solution, fine white crystals of the anhydrous acid were deposited; yield 7.5 g. or 82.5%, m.p. 161–162° (sealed tube).

Anal. Calcd. for $C_5H_{10}O_5S$: C, 32.98, H, 5.71; S, 17.69; neut. equiv., 91.1. Found: C, 32.77; H, 5.71; S, 17.60; neut. equiv., 91.1.

Sulfopivalic Acid Cyclic Anhydride. A.—The acid monohydrate (86 g.) was refluxed with thionyl chloride (100 g.) for 8 hours, then the excess of the latter was removed under reduced pressure. Hot benzene (50 ml.) was added to the residue and the solution thereby obtained was poured slowly with stirring into 400 ml. of cold ligroin. The resulting yellow precipitate was collected on a filter, washed with ligroin and redissolved in hot benzene. The solution was then decolorized with carbon. The pure compound was precipitated by dilution of the decolorized solution with twice its volume of ligroin; yield 48.5 g. or 85%, m.p. 62–64°.

Anal. Calcd. for $C_5H_8O_4S$: C, 36.71; H, 4.94; S, 19.53; neut. equiv., 82.1. Found: C, 36.52; H, 5.05; S, 19.30; neut. equiv., 82.0.

B.—Treatment of pivalic acid (51 g.) with sulfuryl chloride by the method of Kharasch[8] gave the cyclic anhydride of sulfopivalic acid; yield 13 g. or 19.7%, m.p. 62–64°.

Ammonium Salt of Sulfopivalamide.—Sulfopivalic acid cyclic anhydride (10 g.) was added to ammonium hydroxide (28%, 150 ml.) at 5°. The resulting clear solution was evaporated to dryness over steam, and the residue was recrystallized from aqueous alcohol. The white, crystalline solid was quite soluble in water and liberated ammonia when it was treated with a cold solution of sodium carbonate.

This product is analogous to that obtained by Kharasch, *et al.*,[8] by the reaction of sulfopropionic cyclic anhydride with ammonia; hence, it is considered to be the ammonium salt of sulfopivalamide. Analyses substantiate this assumption; yield 13.3 g. or 82%, m.p. 187–188°.

Anal. Calcd. for $C_5H_{14}N_2O_4S$: S, 16.18; N, 14.15. Found: S, 16.04; N, 13.98.

***p*-Toluidine Salt of Sulfopivalo-*p*-toluidide.**—Sulfopivalic acid cyclic anhydride (10 g.) in benzene (30 ml.) was added to a solution of *p*-toluidine (20 g.) in benzene (50 ml.). A vigorous reaction took place. The white solid which formed was separated, washed with benzene and recrystallized from aqueous alcohol; yield 21.8 g. or 76%, m.p. 180–182°.

Anal. Calcd. for $C_{19}H_{26}N_2O_4S$: S, 8.46; N, 7.42. Found: S, 8.71; N, 7.70.

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The Schmidt Reaction. IV. Reaction with α-Methyl-α-ethylbutyrophenone

BY PHILIP J. KOHLBRENNER AND CONRAD SCHUERCH

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Unsymmetrical ketones normally undergo the Schmidt reaction to yield one or two N-substituted amides or their hydrolysis products. However, in the case of compounds containing a tertiary alkyl group, abnormal products may arise in any of three ways: cleavage of the tertiary group to form a car-

bonium ion which itself reacts with hydrazoic acid,[1] as was found to be the case in the reaction of pivalophenone[2]; rearrangement of the carbonium ion before reaction with hydrazoic acid[3]; or rearrangement of the original ketone in the reaction medium to an isomeric ketone.[4] A similar cleavage of tertiary carbonium ions is known to occur in the Beckmann rearrangement.[5,6]

When the Schmidt reaction was carried out in this Laboratory on α-methyl-α-ethylbutyrophenone, the products obtained were analogous to those obtained from pivalophenone.[2] Thus, products resulting from cleavage of a carbonium ion would include benzamide or benzonitrile, which could very likely be hydrolyzed in the reaction medium to benzoic acid and ammonia, as well as the ketimine hydrolysis products: methyl ethyl ketone, diethyl ketone, methylamine and ethylamine. Benzoic acid was isolated in 43% yield, and the above ketones and amines were also recovered.

Products related to either of the possible "normal" N-substituted amides were lacking unless the benzoic acid and the aniline, which was also found, arose from this source. However, there was no evidence for the corresponding tertiary alkyl amine, although α-methyl-α-ethylbutyric acid was most probably present in small quantity. Reaction of the benzoic acid with hydrazoic acid offers an alternative explanation for the formation of aniline.

If the carbonium ion had rearranged before further reaction, acetone and *n*-propylamine would be expected among the products.[3] However, there was no evidence that either of these was present.

Rearrangement of the original ketone by the mechanism recently proposed by Zook and Paviak[4] might lead to the formation of 3-ethyl-3-phenyl-2-pentanone or 4-methyl-4-phenyl-3-hexanone. However, the ketone which was recovered was identical with the starting material.

Experimental

Preparation of α-Methyl-α-ethylbutyrophenone.—Propiophenone (268 g.) in 250 ml. of dry benzene was refluxed five hours with sodamide (from 46 g. of sodium treated with 1000 ml. of liquid ammonia), ethyl bromide (220 g.) was added and stirring continued for 12 hours, following the general method of Haller and Bauer.[7] The product was washed with water, dried and fractionated to yield 240 g. of *sec*-butyl phenyl ketone, b.p. 105–110° at 10 mm. (lit. b.p. 107–109°[7]). The alkylation was repeated with sodamide and ethyl bromide to give 139 g. of a product boiling at 128.5–129° at 11 mm., $n^{24}D$ 1.5123.

Reaction with Hydrazoic Acid.—The ketone (0.1 mole) was dissolved in concentrated sulfuric acid at ice-bath temperature and sodium azide (0.27 mole) was added in small portions while stirring over three hours. The temperature was allowed to rise to 30–40° to maintain a moderate rate of gas evolution.

After complete addition, the acid solution was poured onto 150 g. of ice and the excess acid almost neutralized with sodium hydroxide. An insoluble oily layer was separated, and the water layer steam distilled. The steam distillate was combined with the oil, dried and the 7.5 g. of liquid was fractionated through a Todd column. Methyl ethyl ketone (1.6 g.) was collected at 77–80°; 2,4-dinitrophenylhydrazone m.p. 116–118°, mixed 117°. Diethyl ketone (0.6 g.) was collected at 98–101°; 2,4-dinitrophenylhydrazone m.p. 154–156°, mixed 154–155°. The stillpot residue was fractionated at 10 mm. 1.9 g. of an acid, probably α-methyl-α-ethylbutyric, was collected at 69–75° (α-methyl-α-ethylbutyric acid, b.p. 203–204° at 760 mm.[8]) but no derivative was formed. Unreacted α-methyl-α-ethylbutyrophenone (*ca.* 2.5 g.) was collected at 124–126°; oxime m.p. 119–121°, mixed 119–120°.

The aqueous acid layer was extracted with ether and the ether evaporated. Benzoic acid (4.6 g.) was obtained, m.p. 121–123°, mixed 122–123°; amide m.p. 130–131.5° (benzamide m.p. 130°).[9]

The aqueous layer was made basic and steam distilled into 12 *N* hydrochloric acid. The distillate was evaporated to dryness and yielded 11.5 g. of mixed amine hydrochlorides. The amines were separated by dissolving the hydrochlorides in the minimum volume of concentrated sodium hydroxide, and sweeping the liberated gases over magnesium sulfate and through a series of three traps by a slow air steam. The traps were immersed in (1) salt-ice, (2) carbon tetrachloride at its melting point, (3) Dry Ice–acetone. Concentrated hydrochloric acid was added to each trap and the hydrochloride solutions evaporated to dryness.

Trap 1 contained ethylamine, 1.6 g. as the hydrochloride, N-ethylbenzamide, m.p. 69–70° (lit. 71.5°).[9] Trap 2 contained methylamine, 0.7 g., as the hydrochloride, N-methyl-*p*-toluenesulfonamide, m.p. 72–74° (lit. 75°).[9] Trap 3 presumably contained ammonium chloride, 8.3 g.; it gave no Rimini amine test, and showed no melting or decomposition up to 300°. A non-volatile amine (2 g.) recovered from the surface of the caustic solution was aniline, b.p. 180–185°, N-phenylbenzenesulfonamide, m.p. 110–112° (lit. 112°[9]).

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(2) P. A. S. Smith and J. P. Horwitz, *ibid.*, **72**, 3718 (1950).
(3) C. Schuerch and E. H. Huntress, *ibid.*, **71**, 2238 (1949).
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(5) R. F. Brown, N. M. van Gulick and G. H. Schmid, *ibid.*, **77**, 1094 (1955).
(6) P. D. Bartlett and M. Stiles, *ibid.*, **77**, 2806 (1955).
(7) Haller and Bauer, *Compt. rend.*, **148**, 73 (1909).
(8) Haller and Bauer, *ibid.*, **148**, 127 (1909).
(9) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," T. Y. Crowell Co., New York, N. Y., 1947, pp. 362, 402.

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13-Aza-4,4,8,8,12,12-hexamethyl-2,6,10-trioxatricyclo[7,3,1,$0^{5,13}$]tridecane

BY JOHN W. LYNN

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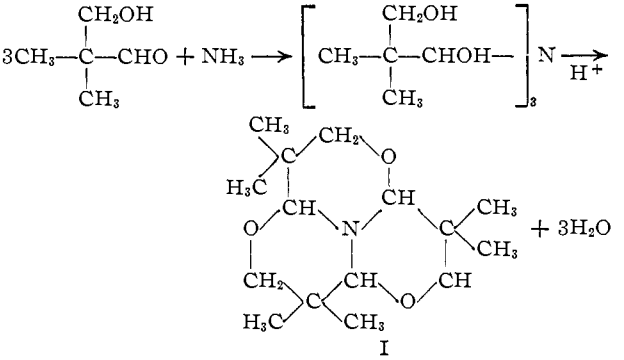
The reaction of 2,2-dimethyl-3-hydroxypropionaldehyde and ammonia followed by acid-catalyzed cyclodehydration gives rise to a novel heterocyclic condensed ring compound, 13-aza-4,4,8,8,12,12-hexamethyl-2,6,10-trioxatricyclo[7,3,1,$0^{5,13}$]tridecane (I).



I

The structure described above has been assigned on the basis of molecular weight, equivalent weight, elemental analysis and infrared spectrum. The ab-