

#### Experimental

**4-Carbomethoxy-4-methylcyclohexene (III).**—A mixture of 100 g. (1.0 mole) of methyl methacrylate, 108 g. (2 moles) of butadiene and 1 g. of hydroquinone<sup>2</sup> was heated in a steel hydrogenation bomb at 180° for fifteen hours. The viscous product was distilled from a Claisen flask under reduced pressure to separate the polymeric materials and the distillate fractionated through a 2 × 40 cm. glass-helix packed column. The yield of III, b. p. 64–65° (10 mm.), *n*<sub>D</sub><sup>20</sup> 1.4600, was 130 g. (84%).

*Anal.* Calcd. for C<sub>9</sub>H<sub>14</sub>O<sub>2</sub>: C, 70.10; H, 9.15. Found: C, 70.34; H, 9.28.

In other runs at 180° for five and six hours, the yields were 64 and 71%, respectively.

Hydrolysis of III with potassium hydroxide gave 4-carboxy-4-methylcyclohexene, m. p. 78–79° after crystallization from ligroin.

*Anal.* Calcd. for C<sub>8</sub>H<sub>12</sub>O<sub>2</sub>: C, 68.55; H, 8.63. Found: C, 68.56; H, 8.63.

**Dimethyl 3-Methyl-3-carbomethoxyadipate (IV).**—A mixture of 145 g. (0.94 mole) of III and 2600 ml. of water was placed in a 12-l. flask equipped with a stirrer, dropping funnel and a thermometer extending close to the bottom of the flask. The contents of the flask were stirred vigorously and a solution of 457 g. (2.3 moles) of sodium permanganate trihydrate in 2600 ml. of water added during four hours. During the addition the reaction mixture was kept saturated with carbon dioxide by adding lumps of Dry Ice every few minutes. The temperature was kept below 50° by external cooling with an ice-bath. The manganese dioxide was reduced by passing in sulfur dioxide, the solution was filtered and extracted with ether in a large continuous extractor for five days. The ether was distilled from the extract and the residue was dried by

(2) Much lower yields (20–55%) were obtained if no hydroquinone was used; cf. Shortridge, Craig, Greenlee, Derfer and Boord, *This Journal*, **70**, 946 (1948), for similar observations.

distillation with benzene using a water separator. The viscous acid remaining after distillation of the benzene was refluxed for three days with 600 g. of methanol containing 2% of dry hydrogen chloride. The excess methanol was distilled, the residue dissolved in ether, and washed with water and sodium carbonate solution. The ethereal solution was dried over magnesium sulfate and distilled through a 30-cm. Vigreux column. The yield of IV was 145 g., b. p. 120–121° (0.7 mm.), *n*<sub>D</sub><sup>20</sup> 1.4443. An additional 9 g. of IV was obtained by esterification of the tribasic acid recovered by acidification and extraction of the sodium carbonate washings of the crude ester. The total yield was 154 g. (70%).

*Anal.* Calcd. for C<sub>9</sub>H<sub>18</sub>O<sub>6</sub>: C, 53.65; H, 7.37; sapon. equiv., 82.1. Found: C, 53.87; H, 7.26; sapon. equiv., 83.7.

**3,5(or 2,3)-Dicarbomethoxy-3-methylcyclopentanone (V).**—The following procedure gave better results than the one used by Ruzicka.<sup>1</sup> In a three-necked creased flask equipped with a stirrer, reflux condenser and dropping funnel was placed 100 ml. of dry toluene, 100 ml. of dry xylene and 3.6 g. (0.15 mole) of clean sodium. The flask was flushed with nitrogen, the contents heated to refluxing and 64 g. (2.0 moles) of methanol added dropwise. After all of the sodium had reacted, 50 ml. of the solvent was distilled to remove most of the excess methanol. To the hot reaction mixture was added 24.6 (0.1 mole) of IV over a forty-five-minute period. The mixture was heated under reflux for two hours, then cooled and 10 ml. of acetic acid added. The mixture was treated with 150 ml. of 1 *N* hydrochloric acid and the organic layer separated, washed with water, sodium carbonate solution and dried over magnesium sulfate. After distillation of the solvent under reduced pressure the residue was fractionated through a short Vigreux column. The yield of V (which may be a mixture of isomers) was 14.6 g. (68%); b. p. 145–151° (7 mm.); *n*<sub>D</sub><sup>20</sup> 1.4628.

*Anal.* Calcd. for C<sub>10</sub>H<sub>14</sub>O<sub>5</sub>: C, 56.07; H, 6.59. Found: C, 56.35; H, 6.83.

**3-Carboxy-3-methylcyclopentanone (VI) and 3-Carbomethoxy-3-methylcyclopentanone.**—The over-all yield of VI, b. p. 140–145° (2 mm.), from IV by the previously reported procedure<sup>1</sup> was 43%. Esterification of VI with methyl iodide instead of ethyl iodide<sup>1</sup> gave 66% of II; b. p. 96° (7.5 mm.), *n*<sub>D</sub><sup>20</sup> 1.4523.

*Anal.* Calcd. for C<sub>8</sub>H<sub>12</sub>O<sub>3</sub>: C, 61.52; H, 7.75. Found: C, 61.34; H, 8.03.

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## The Catalytic Reduction of Dinitroneopentane<sup>1</sup>

BY JACK ROCKETT AND FRANK C. WHITMORE

The reduction of primary aliphatic nitro compounds has been found to yield, other than the primary amines, substances which are presumably reduction intermediates. These are the oxime,<sup>2</sup> the aldimine,<sup>3</sup> the nitrile,<sup>3</sup> and the *N*-hydroxylamine<sup>4</sup> corresponding to the nitro compound.

Among the products resulting from the hydrogenation of dinitroneopentane with Raney nickel catalyst, we have found the expected diamineoneopentane (67%) and, also, the diamide of dimethylmalonic acid (5%). The latter type substance has

(1) This work was completed by J. R. after the untimely death of Dean Frank C. Whitmore. Thanks are due to Dr. Thomas S. Oakwood who served as adviser after the death of Dean Whitmore.

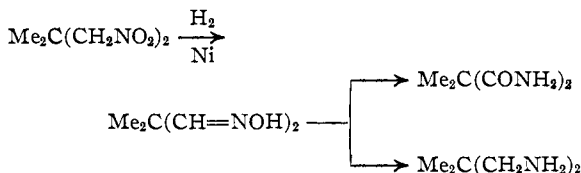
(2) Johnson and Degering, *This Journal*, **61**, 3194 (1939).

(3) Kohler and Drake, *ibid.*, **45**, 1286 (1923).

(4) Hoffman and Meyer, *Ber.*, **24**, 3528 (1891).

not previously been found to result directly from the reduction of a nitro compound.

The work of Paul<sup>5</sup> has demonstrated that aliphatic aldoximes in contact with Raney nickel will spontaneously rearrange upon gentle heating to the corresponding amides. It is therefore likely that some of the intermediate oxime (un-isolated) rearranged in the course of the present reduction



It is possible that the reduction of a nitro compound or an oxime to an amine proceeds by way of the intermediate amide. However, the difficulty of reducing amides to amines<sup>6</sup> would indicate that this is probably not the most important reaction.

#### Experimental

**Reduction of Dinitroneopentane.**—A solution of 97.2 g. (0.6 mole) of dinitroneopentane in 750 ml. of absolute alcohol was placed in a hydrogenation bomb with 6 g. of Raney nickel catalyst. The hydrogenation proceeded at 1000 p. s. i. and 60°, requiring about two hours for completion. The contents of the bomb were placed in a beaker and allowed to stand at room temperature for twenty-four hours. The crystalline material and the catalyst were then filtered, and the crystalline material was removed from the mixture of extraction with hot water. Cooling the hot water solution gave white crystals, m. p. 268–269°, after one recrystallization from water. A second crop of the above compound was obtained by partly evaporating the alcohol from the original reaction mixture.

*Anal.* Calcd. for  $\text{C}_5\text{H}_{10}\text{O}_2\text{N}_2$ : C, 46.15; H, 7.69; N, 21.54. Found: C, 46.54; H, 7.84; N, 21.63.

The compound was shown to be the diamide of dimethylmalonic acid by comparison with a sample of that substance prepared from dimethylmalonic acid through the acid chloride, and subsequent treatment with liquid ammonia.

**Diaminoneopentane.**—The diaminoneopentane from the above reduction was obtained by treating the alcoholic solution above with anhydrous hydrogen chloride, which caused the separation of the di-hydrochloride. The hydrochloride was recrystallized from alcohol, m. p. 256–257°.

*Anal.* Calcd. for  $\text{C}_5\text{H}_{10}\text{N}_2\text{Cl}_2$ : Cl, 40.50. Found: Cl, 40.54.

This compound prepared in another way has been reported as having the m. p. 280–281°. However, the picrate of the compound agreed with that prepared by these authors (m. p. 240°).

The recrystallized hydrochloride was dissolved in 300 ml. of methanol and methanolic potassium hydroxide was added. After filtering the potassium chloride formed, the diaminoneopentane was separated by distillation in an efficient column. It was a mobile water white liquid, fuming in moist air, b. p. 151–153° (737 mm.);  $n_D^{20}$  1.4566.

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(5) R. Paul, *Bull. soc. chim.*, [5] 4, 1115–1121 (1937).

(6) Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wisconsin, 1937.

(7) Komppa and Sevón, *C. A.*, 27, 3914 (1933).

## Evidence for a Solid Dihydrate of Hexafluoroacetylacetone<sup>1</sup>

BY BOYD G. SCHULTZ AND EDWIN M. LARSEN

In the final step in the production of hexafluoroacetylacetone according to the process of Staniforth<sup>2</sup> in which the solvent and product are separated by fractional distillation, we continually obtained a white crystalline residue with corresponding poor yields of the low boiling product.

The white crystalline product was very soluble in ether, slightly soluble in benzene and petroleum ether, and slowly soluble in water. The water solution of this compound was acid to litmus and slowly liberated carbon dioxide from a solution of sodium hydrogen carbonate. It had a pungent odor and was very volatile as evidenced by substantial sublimation occurring even at room temperature. No melting point was observed as the compound sublimed completely before reaching 115°. On the basis of the following experimental results we have concluded that the material obtained is the dihydrate of hexafluoroacetylacetone.

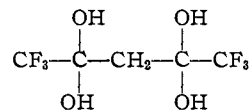
#### Experimental

For analysis the compound was recrystallized from ether, washed with benzene to remove any diketone present, and dried at room temperature under 0.1 mm. pressure. A qualitative elementary analysis confirmed the presence of carbon and fluorine, and the absence of any metallic elements. From the results of the quantitative analysis for carbon,<sup>3</sup> hydrogen<sup>3</sup> and fluorine, the empirical formula of the compound was calculated to be  $\text{C}_5\text{H}_6\text{O}_4\text{F}_6$ .

*Anal.* Calcd. for  $\text{C}_5\text{H}_6\text{O}_4\text{F}_6$ : C, 24.58; H, 2.47; F, 46.71. Found: C, 24.48; H, 2.54; F, 46.3.

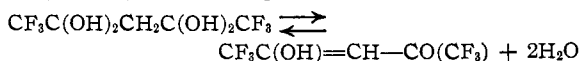
The neutral equivalent of this compound as determined by titration of an aqueous solution with 0.1 N NaOH solution gave a value which corresponded to the molecular weight of the compound,  $\text{C}_5\text{H}_6\text{O}_4\text{F}_6$ : calcd. mol. wt., 244.10; exptl. neutral eq., 245.

Since the fluorine was all present in the starting material as trifluoromethyl groups, it was considered unlikely that the fluorine could be arranged in any other manner, and therefore on the basis of these data it was concluded that this compound was hexafluoroacetylacetone dihydrate



As one would expect, if the proposed formulation were correct, the dihydrate in ether solution was incapable of forming the copper chelate derivative directly. However, a small amount of the enol form must be present in both the ether and water solution of the dihydrate, because on standing in contact with a copper acetate solution for twenty-four hours, a greenish tint, characteristic of the copper chelate, was observed in the ether layer, and after several days the intensity of the coloration increased.

Additional experiments were conducted to test the possibility of dehydration as expressed in the reaction



(1) Based on research carried out under Task Order 4 of Contract N7onr-28504 between the Office of Naval Research and the University of Wisconsin.

(2) Henne, Newman, Quill and Staniforth, *THIS JOURNAL*, 69, 1819 (1947).

(3) Analyses by Clark Microanalytical Laboratory, Urbana, Ill.