

NOTES

The Preparation of *t*-Butylmalonic Acid from Neopentyl Chloride

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The preparation of *t*-butylmalonic acid from *t*-butylacetic acid has been reported recently.¹ Previously an unsuccessful effort had been made to obtain this substance from neopentyl chloride by application of the method of Ivanov and Spassov,² who reported a 60% yield of phenylmalonic acid from benzylmagnesium chloride by carbonating this substance in the usual manner, treating the complex with ethylmagnesium bromide, and carbonating again. Familiarity with the properties of *t*-butylmalonic acid suggested certain modifications in the isolation procedure, and a second attempt to prepare the substance from neopentyl chloride was successful. Although the yield was only 5%, the method may be of sufficient interest to warrant description.

Experimental

The Grignard reagent from 8.88 g. of neopentyl chloride³ was obtained in 120 ml. of ether under nitrogen, and treated with carbon dioxide below -5° , in the usual manner. Part of the ether (60 ml.) was distilled off in a stream of nitrogen. The reaction mixture was treated with 75 ml. of ethylmagnesium bromide in ether (1.64 molar), stirred and refluxed for half an hour, and allowed to stand at $20-25^{\circ}$ for twenty-two hours. The solution was diluted with 40 ml. of ether, refluxed again for one and one-fifth hours, and finally carbonated at -10 to $+4^{\circ}$ during seven-tenths of an hour. The reaction mixture (a thick suspension of granular solid) was decomposed by the addition of 180 ml. of cold 3 molar sulfuric acid. The aqueous layer was extracted three times with 50-ml. portions of pure ether, and the ether solutions were combined and evaporated. The residual liquid (17 g.) dissolved almost completely in 100 ml. of petroleum ether. This solution was extracted with 20-ml. portions of water, each of which was extracted in turn with two equal volumes of ether. Evaporation of the combined ether extracts to dryness left white crystals of impure *t*-butylmalonic acid. In each case the evaporation (at 60°) of the last ml. of liquid appeared to involve removal of *n*-propionic acid. Four extractions of the petroleum ether solution gave, respectively, 700, 200, 60, and 17 mg. of the crude product. One recrystallization from ether-petroleum ether left 760 mg. (5.7% yield) of material having m. p. $153-156^{\circ}$. The malonic acid

was identified by converting it to *t*-butylmalon-*N,N'*-diethylamide, m. p. $151-152^{\circ}$. A mixed melting point with the specimen previously described¹ was the same.

By distillation of the petroleum ether solution remaining from the extractions there was obtained 3 g. (22% yield) of *t*-butylacetic acid. This was identified by conversion to the amide, m. p. $131-132^{\circ}$. A mixed melting point with an authentic specimen was the same.

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NASHVILLE, TENNESSEE RECEIVED FEBRUARY 14, 1939

Composition of a Hydrated Double Salt of Nickel and Potassium Oxalates

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In a recent study of the system nickel oxalate, potassium oxalate and water at 30° , Vosburgh, Israel and Birch¹ demonstrated the formation of a double salt $K_2Ni(C_2O_4)_2 \cdot xH_2O$, but were unable to assign a definite value to the hydration number x . During the course of a similar study, the author prepared a sample of the double salt of sufficient purity to permit an exact determination of the number of molecules of water of crystallization. The preparation of the salt and its analysis were carried out as follows.

A large volume of solution was prepared with the composition 12.44% $K_2C_2O_4$ and 3.53% NiC_2O_4 . Water was removed by placing the solution in a desiccator over calcium chloride. The temperature was maintained carefully at 30° . Crystals of the double salt were deposited slowly until the solution had the composition 23.1% $K_2C_2O_4$ and 3.1% NiC_2O_4 . The crystals were then removed from the solution and quickly pressed between thick layers of filter paper. Three samples were immediately delivered into tared glass-stoppered bottles and weighed. The crystal size (*ca.* 1 mm.) allowed such efficient removal of the mother liquor that the samples lost only 0.3% of moisture upon being air-dried at room temperature. The solid resulting from the evaporation of this small amount of water was assumed to be double salt. The samples were then heated to constant weight at 120° , losing 18.6, 18.7 and 18.9% of water, respectively. The formula $K_2Ni(C_2O_4)_2 \cdot 4H_2O$ corresponds to

(1) Bush, *THIS JOURNAL*, **61**, 637 (1939). This malonic acid was first isolated by Buck and Hjort, *ibid.*, **59**, 2568 (1937).

(2) Ivanov and Spassov, *Bull. soc. chim.*, [4] **49**, 19-23 (1931).

(3) Supplied by the Mallinckrodt Chemical Works.

(1) Vosburgh, Israel and Birch, *THIS JOURNAL*, **58**, 2282 (1936).