

CONDENSATION OF NITROMETHANE AND NITROETHANE WITH ETHYL MALEATE AND FUMARATE IN THE PRESENCE OF POTASSIUM FLUORIDE*

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Abstract—Michael condensations of nitromethane and nitroethane with diethyl fumarate and maleate were carried out in the presence of potassium fluoride as catalyst. Normal reaction products were obtained. When treated with dibutylamine, the products gave dibutylamine nitrite and ethyl esters of itaconic and ethylidenesuccinic acids.

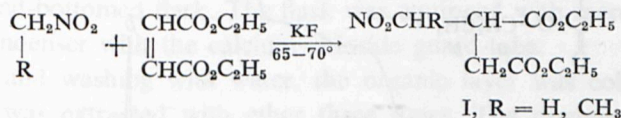
IN THE available literature concerning the Michael reaction no data were found on isolation of the products of condensation of nitromethane and nitroethane with maleic and fumaric acid esters.

Kloetzel^{1,2} has obtained esters of itaconic and ethylidenesuccinic acid by the reaction between esters of the unsaturated acids mentioned above and nitromethane in the presence of diethylamine.

In one of our previous papers³ we described Michael reaction of nitroparaffins with some donors in the presence of potassium fluoride as catalyst. In the present work, potassium fluoride was used in the condensation of nitromethane or nitroethane with ethyl maleate and fumarate.

Diethyl 3-nitropropane-1,2-dicarboxylate and diethyl 3-nitrobutane-1,2-dicarboxylate were obtained, respectively.

They were formed according to the equation:



The I.R. spectra of the compounds reported here show the bands characteristic of the NO₂ group: 1556 cm⁻¹ and 1554 cm⁻¹ (Figs. 1 and 2).

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¹ M. C. Kloetzel, *J. Amer. Chem. Soc.* **70**, 3571 (1948).

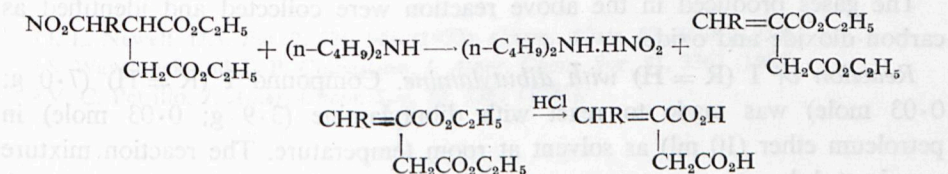
² M. C. Kloetzel, *U. S. Pat.* **2**, 498, 371 (1950); *Chem. Abstr.* **44**, 5384 (1950).

³ A. Ostaszyński and J. Wielgat, *Bull. Acad. Polon. Sci., Sér. Sci. Chim.* **11**, 561 (1963).

The structure of compound I ($R = H$) was confirmed by N.M.R. spectrum measurements (Fig. 3). The chemical shift of the proton in the neighbourhood of the nitro group was found to be $\tau = 5.33$ in agreement with previous investigations of Urbański and co-workers.⁴

The structure of compounds I was established by chemical methods. Hydrolysis of compound I ($R = H$) with 1% hydrochloric acid afforded succinic acid. Alkaline hydrolysis of compounds I, even with dilute aqueous sodium or potassium carbonate, led always to a rapid decomposition of the compound with evolution of nitrogen oxides. For this reason it was impossible to obtain the characteristic reaction for the primary nitro group and the same was probably responsible for the fact that the Michael condensation products could not be isolated from the alkaline medium.

On treatment of compounds I ($R = H, CH_3$) with dibutylamine at room temperature the molecule of nitrous acid was split off and the dibutylamine nitrite was formed in 91% yield. Itaconic or ethylidenesuccinic acid esters were isolated from the reaction mixture and then hydrolyzed to free acids.



The same reaction took place with dihexylamine.

EXPERIMENTAL

All melting points are uncorrected. I.R. spectra were measured on a Hilger H-800 spectrometer with sodium chloride optics.

Diethyl 3-nitropropane-1,2-dicarboxylate (I, $R = H$). Nitromethane (6.1 g; 0.1 mole), commercial anhydrous potassium fluoride (3.0 g; 0.05 mole), and diethyl maleate or fumarate (17.2 g; 0.1 mole) were heated 10 hr at 65–70° in a 100-ml, round-bottomed flask. The flask was equipped with mercury-sealed stirrer, and a condenser with the calcium chloride guard-tube.

After cooling and washing with water, the organic layer was collected and the water layer was extracted with ether three times. The organic layer and ether extract were combined and dried over anhydrous magnesium sulphate. The final products were distilled under reduced pressure and most of the unchanged reactants were removed. Diethyl 3-nitropropane-1,2-dicarboxylate (6.0 g; 25.7%) distilled in a CO_2 atmosphere at 118–120°/0.4 mm, n_D^{27} 1.4405.

⁴ W. Hofman, L. Stefaniak, T. Urbański and M. Witanowski, *J. Amer. Chem. Soc.* **86**, 554 (1964).

(Found: C, 46.13; H, 6.80; N, 6.63; mol. w. 231, 234. $C_9H_{15}O_6N$ requires: C, 46.35; H, 6.48; N, 6.01%; mol. w. 233).

Diethyl 3-nitrobutane-1,2-dicarboxylate (I, $R = CH_3$). The reaction of nitroethane (15.0 g; 0.2 mole) with diethyl maleate (34.4 g; 0.2 mole) in the presence of commercial anhydrous potassium fluoride (15.0 g; 0.25 mole) was carried out in the same manner as the condensation of nitromethane with diethyl maleate. A colourless oil (22.5 g; 45.5%) b.p. 119–121°/0.4 mm, n_D^{27} 1.4413, was obtained. (Found: C, 48.80; H, 7.35; N, 6.01. $C_{10}H_{17}O_6N$ requires: C, 48.58; H, 6.93; N, 5.67%).

Hydrolysis of I (R = H) with hydrochloric acid. Compound I ($R = H$), (9.3 g; 0.04 mole) was refluxed 7 hr with 1% hydrochloric acid (100 ml).

The mother liquor was concentrated to a volume of 10 ml. Succinic acid, the final product, was crystallized repeatedly from water, m.p. 183–184° (4.3 g; 91.5%), reported⁵ 183–184°. (Found: C, 40.42; H, 5.36%. Calcd. for $C_4H_6O_4$: C, 40.6; H, 5.1%). The m.p. was undepressed by admixture with commercial succinic acid.

The gases produced in the above reaction were collected and identified as carbon dioxide and oxide.

Reaction of I (R = H) with dibutylamine. Compound I ($R = H$) (7.0 g; 0.03 mole) was made to react with dibutylamine (3.9 g; 0.03 mole) in petroleum ether (10 ml) as solvent at room temperature. The reaction mixture was kept 1 hr at room temperature. Dibutylammonium nitrite was separated, the mother liquor was washed with water, 10% hydrochloric acid and with water again. The product was dried over $MgSO_4$ and distilled *in vacuo*, b.p. 76–78°/1.4 mm. Itaconic ethyl ester (3.0 g; 53.64%) was obtained in the form of an oil,¹ n_D^{26} 1.4380. (Found: C, 57.80; H, 7.79%. Calcd. for $C_9H_{15}O_4$: C, 58.04; H, 7.70%).

Diethyl itaconate (1 g) was heated with 10% hydrochloric acid (10 ml) for 5 hr at 65–70°. The reaction mixture was concentrated by evaporation *in vacuo*. Itaconic acid (0.4 g; 57.8%), m.p. 164–165°, (reported⁶ 164–165°), was obtained. (Found: C, 45.91; H, 5.34%. Calcd. for $C_5H_7O_4$: C, 45.80; H, 5.38%).

Reaction of I (R = CH_3) with dibutylamine. Dibutylamine (3.4 g; 0.26 mole) and I ($R = CH_3$) (6.5 g; 0.026 mole) were mixed together and kept at room temperature for 12 hr. Subsequently petroleum ether (10 ml) was added. Isolation of the products was carried out as for compound I ($R = H$). Diethyl ethylidene succinate¹ (3.6 g; 67.9%), b.p. 83–85°/0.9 mm, n_D^{27} 1.4448, was obtained. (Found: C, 59.72; H, 8.15%. Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05%).

⁵ H. Marshall and A. Th. Cameron, *J. Chem. Soc.* 1519 (1907).

⁶ J. L. Simonsen, *J. Chem. Soc.* 783 (1915).

Dibutylammonium nitrite was recrystallized from toluene, m.p. 128–129° (reported⁷ 128–129°). The product can be purified by sublimation at 82–85°/1 mm. (Found: N, 16.1%. Calcd. for $C_8H_{20}O_2N_2$: N, 15.9%).

N-nitrosodibutylamine. Dibutylammonium nitrite (7.5 g; 0.043 mole) was heated on an oil bath at 135° for 20 min. In the course of the reaction water was evolved. Crude product was extracted with ether, and the water layer was separated. The ethereal extract was dried over $MgSO_4$ then the ether was removed and the final product was distilled *in vacuo* at 80–82°/1.3 mm. *N*-nitrosodibutylamine⁸ (5.9 g; 87.6%) was obtained, n_D^{26} 1.4433. (Found: N, 17.97% Calcd. for $C_8H_{18}ON_2$: N, 17.7%).

Reaction of compound 1 with dihexylamine. Dihexylammonium nitrite was obtained in 90% yield on the same route as the dibutylammonium nitrite described above. The product was crystallized from toluene, m.p. 136–137° (reported⁹ 136–137°). (Found: N, 11.9%. Calcd. for $C_{12}H_{28}O_2N_2$: N, 12.0%).

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⁷ I. L. Newell, *U.S. Pat.* 2, 626, 968 (1953); *Chem. Abstr.* 47, 4648 (1953).

⁸ S. Wawzonek and T. P. Culbertson, *J. Amer. Chem. Soc.* 81, 3367 (1959).

⁹ V. C. Petrillo, *J. Amer. Chem. Soc.* 73, 2381 (1951).

