When mercury(I) nitrate was added to a dilute solution of orthophosphoric acid, a pure white crystalline precipitate was obtained which did not change color. The precipitate was filtered, washed with water and dried in a desiccator over anhydrous calcium chloride.

Anal. Calcd. for Hg_2HPO_4: Hg, 80.71. Found: Hg, 79.2, 80.8.

The various concentrations of phosphoric acid were made by diluting a stock solution which had been prepared from 85% acid and standardized by titration against standard sodium hydroxide using thymolphthalein as indicator.

The platinized platinum electrodes were prepared with the usual care. Several were used and they checked with each other to within 0.3 millivolt. The hydrogen was bubbled through a solution of chromous chloride acidified with acetic acid[4] to remove oxygen, then through a solution of phosphoric acid of the same concentration as that used in the cell. The cell was H-shaped with a sintered glass diaphragm in the horizontal arm. Potentials were measured with a Rubicon, type B, potentiometer at 25 ± 0.05°.

The cells made with the yellow tertiary mercurous phosphate did not give constant or reproducible potentials. In all cases the potential would decrease with time and approach a minimum value. In some cases the yellow phosphate had changed to a white color in the 0.2 *M* phosphoric acid after several days. Typical potentials were 0.7364, 0.7392 and 0.7492 decreasing to 0.7245, 0.7228 and 0.7313 after seven days.

The cells made with the white secondary mercurous phosphate gave fairly constant and reproducible results and equilibrium values were established within one day. For the cell H_2 ($a = 1$), $H_3PO_4(m)$, $Hg_2HPO_4(s)$, Hg, the cell reaction is $H_2 + Hg_2HPO_4 = H^+ + H_2PO_4^- + Hg$, and if the secondary and tertiary ionizations are assumed to be negligible, the potential at 25° is given by the equation $E = E^0 - 0.02957 \log a_{H^+}a_{H_2PO_4^-}$. For $a_{H^+}a_{H_2PO_4^-} = K_1a_{H_3PO_4}$, the value of $K_1 = 7.516 \times 10^{-3}$ was used as reported by Nims.[5] The activities of the undissociated phosphoric acid were taken from the results of Mason and Blum.[6] The calculated molal standard potential of the cell is given in the last column of Table I. The E^0 for the most dilute solution does not agree with the other values. Excluding that value, the average is 0.639 ± 0.002 volt.

An independent calculation for the E^0 of the cell can be made by using the Debye–Hückel limiting law for the mean ion activity coefficient of phosphoric acid and by using the degree of dissociation, α, tabulated by Mason and Blum,[6] to calculate the concentration, m_1, of the hydrogen and the dihydrogen phosphate ion. The previous equation becomes $E^{0\prime} = E + 0.05914 \log \alpha m = E^0 + 0.0301\sqrt{\alpha m}$, using $\log \gamma_{\pm} = -0.5085\sqrt{\mu}$ and $\mu = m_1 = \alpha m$. The results of such a calculation are given in Table II. The average value of 0.638 ± 0.002 for the E^0 of the cell agrees better than one should expect. The molal potential for the electrode Hg, Hg_2HPO_4, $H_2PO_4^-$ is -0.639 ± 0.002 volt at 25°.

TABLE I

POTENTIAL OF CELLS AND CALCULATION OF STANDARD POTENTIAL, E^0, OF THE CELL

m	E		$a_{H_3PO_4}$	$E^0_{298.1}$
0.001026	0.7998	0.7995	0.0001050	0.6191
.01026	.7730	.7750	.004204	.6409
.02052	.7601	.7600	.01223	.6406
.05130	.7433	.7453	.03440	.6382
.1032	.7341	.7336	.08057	.6388
.2071	.7215	.7221	.1776	.6368

TABLE II

STANDARD POTENTIAL CALCULATED FROM DEGREE OF IONIZATION DATA

m	α	E	$E^{0\prime}$	E^0
0.01026	0.599	0.7740	0.6432	0.6400
.02052	.492	.7600	.6421	.6378
.05130	.366	.7443	.6423	.6365
.1032	.290	.7339	.6438	.6365

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[4] Stone and Skavinski, *Ind. Eng. Chem., Anal. Ed.*, **17**, 495 (1945).

[5] Nims, THIS JOURNAL, **56**, 1110 (1934).

[6] Mason and Blum, *ibid.*, **69**, 1246 (1947).

The Ziegler Bromination of Ethyl Tetrolate

BY J. ENGLISH, JR., AND J. DELAFIELD GREGORY[1]

In a recent review article Djerassi[2] commented on the lack of data on the reactions of N-bromosuccinimide with acetylenic compounds. This prompts us to record our observations on the bromination of ethyl tetrolate by this method.

Tetrolic acid was synthesized by the action of carbon dioxide on propynylmagnesium bromide and converted to its ethyl ester in the usual manner.[3] Pure samples of the ester were then dissolved in carbon tetrachloride and treated with N-bromosuccinimide at reflux temperatures, with addition of benzoyl peroxide, under ultraviolet light, without either, and finally in a sealed vessel at 150°. In all cases most of the ester was recovered unchanged. The only product that could be isolated in pure form was ethyl α,β-dibromocrotonate, resulting apparently from the addition of two atoms of bromine at the triple bond.

A somewhat analogous addition reaction accompanying the Ziegler bromination of cyclobutene and methylene cyclobutane has been reported by Buchman and Howton.[4] In the present instance, although no hydrogen bromide was noted, the rather extensive decomposition observed might well have produced some of this substance and hence made bromine available to the reaction mixture as pointed out by these authors.

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[2] C. Djerassi, *Chem. Rev.*, **43**, 296 (1948); see also A. Wohl and K. Jachinowski, *Ber.*, **54**, 476 (1921).

[3] Stolz, communication cited in Beilstein, II, p. 480.

[4] E. R. Buchman and D. R. Howton, THIS JOURNAL, **70**, 2517, 3510 (1948).

Experimental

A suspension of 19.5 g. of N-bromosuccinimide in 30 cc. of carbon tetrachloride was mixed with 12.0 g. of ethyl tetrolate and 0.5 g. of freshly recrystallized dibenzoyl peroxide. After fifty minutes at reflux temperature the pale yellow solution was decanted from 15 g. of dark tarry material, the solvent evaporated and the residue distilled. In addition to 6.6 g. (55%) of ethyl tetrolate there was obtained 3.5 g. (12%) of a fraction boiling at 68–75° at 2 mm. This product was combined with those from other experiments and carefully fractionated to yield pure ethyl α,β-dibromocrotonate b. p. 58.5–60° at 0.8 mm., n^{20}_{D} 1.5175, d^{20}_{4} 1.744.

Anal. Calcd. for $C_6H_8O_2Br_2$: C, 26.50; H, 2.96; Br, 58.77. Found: C, 26.60; H, 3.05; Br, 58.62.

For further identification a sample was saponified by refluxing with 10% aqueous potassium hydroxide. From the highly colored product there was isolated by extraction with ligroin pure α,β-dibromocrotonic acid, m. p. 118.5–119.5°. Michael reported the melting point of this substance as 120°.[5]

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[5] A. Michael, *Ber.*, **34**, 4221 (1901).

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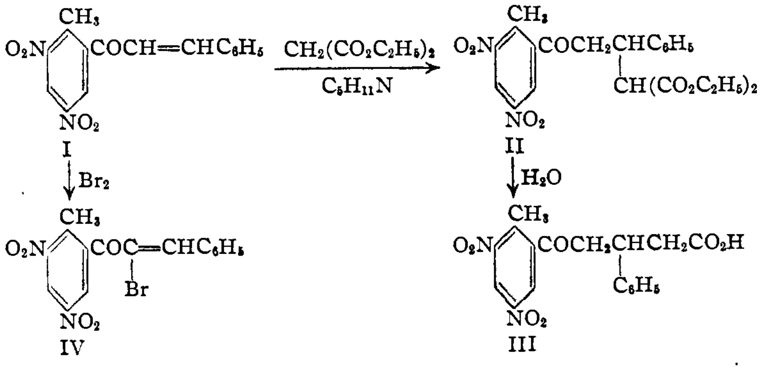
The Condensation of 2'-Methyl-3',5'-dinitrochalcone with Ethyl Malonate

BY REYNOLD C. FUSON AND GEORGE MUNN

2'-Methyl-3',5'-dinitrochalcone (I) was prepared in the hope that it might undergo an intramolecular Michael condensation to yield the corresponding substituted α-tetralone. However, under the conditions ordinarily employed for Michael condensations no ring closure occurred. That this chalcone is capable of undergoing reactions of the Michael type was demonstrated by condensing it intermolecularly with ethyl malonate.

The product (II) which was obtained when the chalcone was allowed to react with ethyl malonate was hydrolyzed and the resulting acid decarboxylated to form 2-phenyl-3-(2-methyl-3,5-dinitrobenzoyl)-butyric acid (III).



The 2'-methyl-3',5'-dinitrochalcone yielded a monobromo derivative when it was allowed to react with bromine in acetic acid solution. Oxidation of the bromochalcone with permanganate produced 3,5-dinitro-*o*-toluic acid, showing that the bromine was not attached to the methyl group. It thus seems probable that the addition of bromine to the double bond is followed by the loss of hydrogen bromide, forming 2'-methyl-3',5'-dinitro-α-bromochalcone (IV).

Experimental

2-Methyl-3,5-dinitroacetophenone.—2-Methyl-3,5-dinitrobenzoyl chloride was prepared by heating a mixture of 45 g. of 3,5-dinitro-*o*-toluic acid,[1] 35 ml. of purified thionyl chloride, and 200 ml. of dry benzene under reflux until the acid completely dissolved. The solvents were then removed by distillation under diminished pressure, and the residue was dissolved in 250 ml. of dry ether. This ether solution was used without further purification.

An ether solution of the ethoxymagnesium salt[2] of malonic ester was made in the following manner: Five milliliters of absolute ethanol, 0.5 ml. of carbon tetrachloride, and 5.25 g. of magnesium turnings were placed in a flask and allowed to react for a few minutes. Seventy-five milliliters of anhydrous ether was then added and to this mixture a solution of 35.2 g. of ethyl malonate, 20 ml. of absolute ethanol and 25 ml. of dry ether was added at a rate such that mild refluxing was maintained.

When the magnesium had dissolved, the solution of 2-methyl-3,5-dinitrobenzoyl chloride was added with stirring over a period of thirty minutes. The contents of the flask were then heated under reflux for an additional thirty minutes and then acidified with dilute sulfuric acid. The ether layer and an ether extract of the water layer were combined and the solvent was removed by distillation. The residual liquid was heated under reflux for four hours in a mixture of 60 ml. of acetic acid, 7.5 ml. of concentrated sulfuric acid and 40 ml. of water. The mixture was cooled, diluted with water and extracted with ether. The ether was washed with sodium bicarbonate solution, dried over calcium chloride, and the solvent was removed by distillation. The residue was distilled under diminished pressure at 150–152° (2 mm.). The yield was 27 g. (60%). When recrystallized from methanol, the 2-methyl-3,5-dinitroacetophenone melted at 72–73°.

Anal. Calcd. for $C_9H_8N_2O_5$: C, 48.24; H, 3.60; N, 12.50. Found: C, 48.47; H, 3.79; N, 12.40.

2'-Methyl-3',5'-dinitrochalcone (I).—Dry hydrogen chloride was bubbled slowly over a period of two days into a solution of 22.6 g. of 2-methyl-3,5-dinitroacetophenone and 12 ml. of benzaldehyde in 150 ml. of glacial acetic acid. During this time a crystalline precipitate appeared. The mixture was then heated under reflux for two hours and poured on ice. The white precipitate which formed was collected on a filter and recrystallized from ethanol. Twenty-one grams of 2'-methyl-3',5'-dinitrochalcone was obtained; m. p. 128–129°; 67%.

Anal. Calcd. for $C_{16}H_{12}N_2O_5$: C, 61.53; H, 3.88; Found: C, 61.65; H, 3.90.

Condensation of 2'-Methyl-3',5'-dinitrochalcone with Ethyl Malonate.—A mixture of 3.1 g. of 2'-methyl-3',5'-dinitrochalcone, 2 ml. of ethyl malonate, 100 ml. of absolute ethanol, and 5 drops of piperidine was heated under reflux for twenty-four hours. It was then diluted with water, acidified and extracted with ether. The ether layer was dried over calcium chloride, and the solvent was removed by distillation. The residue was recrystallized several times from methanol with the use of charcoal; 1.8 g. of white crystals (II) was obtained; m. p. 96–97°.

Anal. Calcd. for $C_{23}H_{24}N_2O_9$: C, 58.47; H, 5.12; N, 5.93. Found: C, 58.78; H, 5.16; N, 6.09.

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[1] McGookin, Swift and Tittensor, *J. Soc. Chem. Ind.* (*Trans.*), **59**, 92 (1940).

[2] Walker and Hauser, THIS JOURNAL, **68**, 1386 (1946).