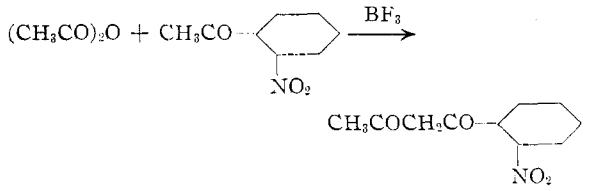
factory; this has been verified. Yields of 64–68% of the *o*-, *m*- and *p*-nitrobenzoylacetones have been obtained from the corresponding nitroacetophenones. The acetylation of *o*-nitroacetophenone may be represented as



Since the nitroacetophenones are readily prepared,[5] the present method for preparing the nitro β-diketones is considered quite convenient.[6]

Gabriel and Gerhard[7] have reported that *o*-nitrobenzoylacetone is reduced and cyclized in the presence of phosphorus and hydrogen iodide, or stannous chloride and acetic acid, to form 2-methyl-4-hydroxy-quinoline oxide. McCluskey[8] found that this nitrogen oxide is converted to 2-methyl-4-hydroxy-quinoline on boiling with zinc dust and hydrochloric acid. We have found that the nitrogen oxide is similarly obtained from *o*-nitrobenzoylacetone using low pressure hydrogenation at 60° in the presence of Raney nickel or at room temperature using palladium charcoal (experiment by M. S. Bloom).

Experimental[9]

m-Nitroacetophenone (0.1 mole) was dissolved in 70 ml. (about 0.7 mole) of acetic anhydride, and the stirred mixture was saturated at 0° with boron trifluoride as described previously for similar acylations.[4b] Then 700 ml. of 13% sodium acetate solution was added and the resulting mixture refluxed for twenty minutes. The mixture was chilled in an ice-bath and filtered. The precipitate was washed thoroughly with water, crushed in a mortar and dissolved in 300 ml. of cold 2% sodium hydroxide solution. The alkaline solution was shaken with ether. The ether phase was extracted with additional 2% alkali until it no longer gave a positive enol test. After filtering, the combined alkaline solution was chilled in an ice-bath and acidified with 10% sulfuric acid. The solid *m*-nitrobenzoylacetone was filtered off and recrystallized from 95% ethanol; yield, 64% melting at 113.5–114.5°[2]; m. p. of copper salt, 277–278°.

In a similar manner, we prepared *p*-nitrobenzoylacetone in 66% yield, melting at 111.4–112.6° and after a second recrystallization at 112.0–112.8°[2] (the copper salt darkened but failed to melt at 320°); also, we prepared *o*-nitrobenzoylacetone in 68% yield melting at 54–55°[6] (catalytic reduction gave 2-methyl-4-hydroxyquinoline oxide, melting at 245–246°).[8]

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(5) See Walker and Hauser, THIS JOURNAL, **68**, 1387 (1946).

(6) *m*-Nitrobenzoylacetone has been prepared in 47% yield by the nitration of benzoylacetone (see reference 2). *o*-Nitrobenzoylacetone has been prepared by the acylation of acetoacetic ester with *o*-nitrobenzoyl chloride followed by abidic cleavage [Gevekoht, *Ann.*, **221**, 323 (1883), and Kermack and Smith, *J. Chem. Soc.*, 814 (1929)].

(7) Gabriel and Gerhard, *Ber.*, **54**, 1067 and 1615 (1921).

(8) McCluskey, THIS JOURNAL, **44**, 1577 (1922).

(9) Melting points are uncorrected.

The Inhalation Toxicity of Ketene and of Ketene Dimer

BY H. A. WOOSTER,[1] C. C. LUSHBAUGH AND C. E. REDEMAN[2]

The literature concerning the use of ketene in organic syntheses stresses its irritant qualities,[3,4] but contains no detailed statement of its toxicity. Preliminary tests indicated that freshly generated ketene was highly toxic.[5]

Extended toxicity testing on mice, rats, guinea pigs and rabbits showed that ten minute exposures to concentrations of freshly generated ketene as low as 0.2 mg./liter (116 p. p. m.) may produce a high percentage of deaths in small animals. Diketene is less than 0.1 as toxic. These findings put ketene in the same order of toxicity as phosgene[4] (0.2–2.0 mg./liter) and hydrogen cyanide[6] (0.2–0.5 mg./liter). Death is from pulmonary edema and is entirely similar to, but much more rapid than is the case with phosgene poisoning. A complete report of this study will be made elsewhere.

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(3) N. T. M. Wilsmore, *J. Chem. Soc.*, **91**, 1938 (1907).

(4) C. D. Hurd and O. Kamm, "Organic Syntheses," Vol. IV, John Wiley and Sons, Inc., 1925, pp. 39–42.

(5) R. W. Gerard and W. Potts, personal communication.

(6) M. B. Jacobs, "Analytical Chemistry of Industrial Poisons, etc.," Interscience Publishers, Inc., 1941, p. 622.

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Direct Replacement of the Mesyloxy[1] Group by Cyanide

BY MORRIS ZIEF, HEWITT G. FLETCHER, JR., AND HOWARD R. KIRSHEN

In the course of the preparation of several organic cyanides, our first approach to the synthesis of tetrahydrofurylacetonitrile by the replacement of the tosyloxy[1] group, followed the method described by Sekera and Marvel[1a] for the preparation of *n*-cetyl cyanide and *n*-butyl cyanide. After this procedure failed, the fusion method suggested by the familiar reaction for the preparation of aryl cyanides by the fusion of the salts of aromatic sulfonic acids with potassium cyanide[2] proved successful. Fusion of tetrahydrofurfuryl tosylate with potassium cyanide produced a nine per cent. yield of the nitrile. When the mesyloxy[1] group, which in most instances has been shown to be more labile than the tosyloxy group,[3] was substituted for the tosyloxy group, a 36% yield was obtained. When 6-tosyldiacetonegalactose, *n*-butyl tosylate or mesylate was fused with potassium cyanide, no reaction was observed. *s*-Butyl mesylate yielded considerable butene-2.

(1) "Tosyl" and "mesyl" are generally accepted abbreviations for *p*-toluenesulfonyl and methanesulfonyl, respectively.

(1a) Sekera and Marvel, THIS JOURNAL, **55**, 348 (1933).

(2) Merz and Mulhauser, *Ber.*, **3**, 710 (1870).

(3) Helferich and Gnuchtel, *ibid.*, **71**, 712 (1938).