TABLE II

Reflux time, hr.	Bitetrazole, g. (%)	5-Dinitromethyltetrazole, g. (%)	Recovered ammonium dinitroacetonitrile, g. (%)
24	0.68 (8.0)	1.07 (12.3) from 2.1 g. of crude	5.37 (71.8)
48	1.80 (21.9)	0.80 (9.2) from 2.7 g. of crude	2.64 (35.2)

A reaction using 0.05 mole of ammonium dinitroacetonitrile, 0.051 mole of sodium azide, and 0.0051 mole of ammonium chloride (10 mole % of the sodium azide) in 25 ml. of water refluxed for 24 hr. gave 0.34 g. (4.0%) of bitetrazole and 0.2 g. (2.3%) of crude 5-dinitromethyltetrazole.

After 24 hr. of refluxing, the reaction mixture gave a positive test for the presence in large concentration of cyanide ion with benzidine–copper acetate reagent.[17]

Elementary analyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Acknowledgment.—The author gratefully acknowledges the many helpful suggestions made by Dr. G. P. Sollott of this laboratory in reviewing this paper and the helpful discussions with Drs. R. A. Henry and W. G. Finnegan of the Naval Ordnance Test Station.

(17) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1957, pp. 174, 175.

The Synthesis of 1-Aryl 3-Cyano-5-pyrazolones

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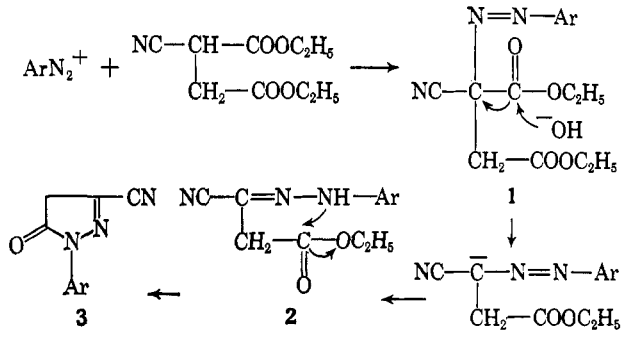
Received January 20, 1964

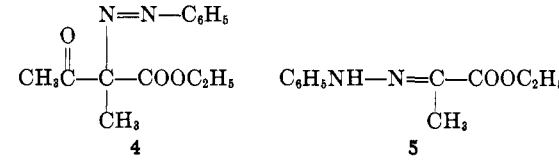
Kendall and Fry[1] reported a method for the preparation of certain 1-aryl 3-substituted pyrazolones by the reaction of diazotized aromatic amines with the appropriately substituted diethyl succinates in an alkaline medium. While this suggested a convenient procedure for 3-cyanopyrazolones, in the single example describing the use of diethyl cyanosuccinate,[2] only the 3-carboxy compound was isolated, presumably because the alkaline conditions used for the ring closure also led to hydrolysis of the cyano group.[3]

As suggested by Kendall and Fry, the reaction may be considered to be a three-step process. The initially formed azo compound **1** loses the carbethoxyl group to give an intermediate which tautomerizes to the phenylhydrazone **2**. This then cyclizes to the pyrazolone **3** (see col. 2).

Recently Yao and Resnick[4] have reported the isolation and spectral properties of intermediates analogous to **1** and **2**. Thus, ethyl α-phenylazo-α-methylacetoacetate (**4**) had a λ_{max} of 272 mμ and ethylpyruvate phenylhydrazone (**5**) had absorption maxima at 290 and 312 mμ. These findings suggested that the reaction of diazonium salts with diethyl cyanosuccinate



could be followed by ultraviolet spectroscopy, and that, thereby, sufficiently mild conditions for the ring closure might be found which would permit the isolation of the desired 3-cyanopyrazolones.



When diazotized *p*-toluidine was added to diethyl cyanosuccinate in pyridine, an immediate yellow color appeared. Examination of the ultraviolet spectrum in ethanol of samples obtained by precipitating aliquots of the solution into aqueous hydrochloric acid showed the presence of strong absorption at 296 mμ, presumably due to **1**. Even on several hours standing, the reaction mixture showed no further changes. Addition of triethylamine caused the very slow, but never complete, diminution in the intensity of the 296 mμ peak, and the slow increase of broad absorption at 300–350 mμ (**2**?). However, addition of a mixture of triethylamine and 2% sodium hydroxide solution caused a rapid drop in the 296-mμ peak, transient broad absorption at 300–350 mμ, and the appearance of a new strong band centered at 254 mμ due to **3**. After 1 hr., no further significant changes were observed.

The procedure as described below appears to be a general one for the preparation of 1-aryl 3-cyanopyrazolones in reasonable yields from the corresponding aryl amines. The crude products made by this procedure were usually contaminated with traces of a yellow impurity. This is believed to be due to the presence of small amounts of aryl azopyrazolone formed by the reaction of **3** with traces of unconsumed diazonium salt. The use of an excess of diethyl cyanosuccinate suppresses the formation of this impurity which is easily removed during the work-up.

Experimental[5]

1-*p*-Tolyl-3-cyano-5-pyrazolone.—To a solution of 0.0375 mole of diethyl cyanosuccinate[6] in 175 ml. of pyridine was added a solution of the diazonium salt prepared by diazotizing, at 0–5°, 0.025 mole of *p*-toluidine in 50 ml. of water and 6 ml. of concentrated hydrochloric acid with 1.75 g. of sodium nitrite dissolved in 10 ml. of water. After the mixture had been stirred at 20° for 20 min., 50 ml. of triethylamine and 100 ml. of 2% aqueous

(1) (a) J. D. Kendall and D. J. Fry, British Patent 585,780 (1947); *Chem. Abstr.*, **42**, 224*b* (1948). (b) See also U. S. Patent 2,459,226 (1949); *Chem. Abstr.*, **43**, 3042*h* (1949).

(2) Ref. 1a, example 8 in patent.

(3) This may also have resulted *via* displacement of the cyano group rather than the carbethoxyl group from the intermediate azo compound.

(4) H. C. Yao and P. Resnick, *J. Am. Chem. Soc.*, **84**, 3514 (1962).

(5) Melting points are uncorrected and were obtained on a Mel-Temp capillary melting point apparatus. Elemental analyses were by Dr. S. M. Nagy of the Microchemical Laboratory, Massachusetts Institute of Technology. Ultraviolet spectra were determined using a Cary Model 11 spectrophotometer. Infrared spectra were determined on potassium bromide disks using a Perkin-Elmer Model 421 spectrophotometer.

(6) A. Haller and L. Barthe, *Compt. rend.*, **106**, 1413 (1888).

sodium hydroxide was added. The solution was stirred for 1.5 hr. and then poured into 400 ml. of concentrated hydrochloric acid and 1 kg. of ice. The resulting creamy solid was collected by suction filtration, washed with water, dissolved in 125 ml. of cold 2% sodium hydroxide solution, and extracted with three 50-ml. portions of ether to remove traces of an orange impurity. The solid obtained on acidification of the aqueous solution with 5% hydrochloric acid was collected and crystallized from acetic acid to give 3.15 g. (64%) of light tan crystals, m.p. 209–210° dec.; ultraviolet spectrum: λ_{max} 255 mμ (ϵ 16,000), shoulder at *ca.* 310 mμ (EtOH); infrared spectrum: very sharp absorption at 2248 cm.$^{-1}$ (C≡N).

Anal. Calcd. for $C_{11}H_9N_3O$: C, 66.32; H, 4.55; N, 21.10. Found: C, 66.41; H, 4.52; N, 20.98.

In a similar fashion, the following aromatic amines were converted to the corresponding 1-aryl 3-cyanopyrazolones: *p*-ethylaniline (58%), m.p. 172–173° dec. (benzene); *p*-aminophenethyl alcohol (47%), m.p. 147–148° dec. (nitromethane); and *m*-aminobenzotrifluoride (64%), m.p. 117–120° (1,2-dichloroethane). Satisfactory analyses were obtained for all compounds.

Acknowledgment.—We wish to thank Dr. T. W. Milligan for helpful discussions and suggestions made during the course of this work.

Reactions of Cupric Bromide in Dioxane. Formation of ω-Bromo-*o*-hydroxyacetophenone

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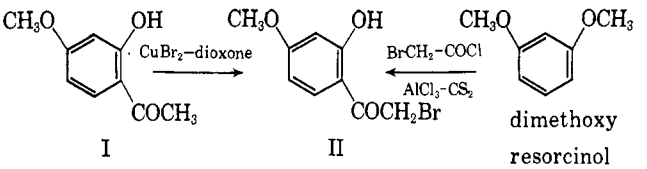
Received January 4, 1963

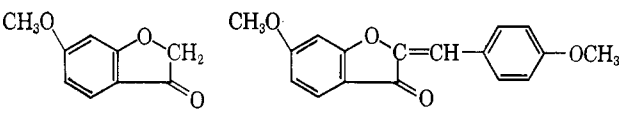
That cupric bromide acts as a brominating agent is not new to the organic chemists. Aliphatic ketones,[1] aliphatic aldehydes,[2] and cyclohexanone[3] have been successfully brominated with cupric bromide in methanol, aqueous methanol, or toluene at the α-carbon atom. Recently, 17-oxoandrostane or its 17-enol acetate has been shown to give 16-α-bromo-17-oxoandrostane[4] with cupric bromide.

The present work deals with the action of cupric bromide in dioxane on *o*-hydroxyacetophenone and on some of its derivatives. When *o*-hydroxyacetophenone is brominated with reagents like bromine in acetic acid, ether, carbon tetrachloride, dioxane,[5] or aqueous acetic acid,[6] or with N-bromosuccinimide (NBS) or pyridine bromine complex,[7] nuclear bromination takes place. 4-Methoxy-2-hydroxyacetophenone (I) with cupric bromide in dioxane under reflux temperature gave a bromo compound (II), m.p. 161°. On analysis, II was found to be $C_9H_9BrO_3$. It was not identical with 5-bromo-4-methoxy-2-hydroxyacetophenone, m.p. 82°.

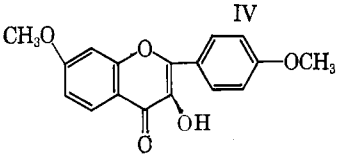
II gave I on treatment with zinc dust in an aqueous medium,[8] an acetoxy derivative *via* an iodo derivative, coumaran-3-one (III) with base,[9] benzal coumaran-3-one (IV) or flavonol V on condensation with an aromatic aldehyde in an alkaline medium,[10] and a rose red color with alcoholic potash. (Rose red coloration with alcoholic potassium hydroxide indicates a labile bromine atom which effects ring closure with an elimination of hydrogen bromide giving a benzofuran-3-one derivative.) These reactions clearly show that bromination has taken place at the ω-position and II is ω-bromo-4-methoxy-2-hydroxyacetophenone. This was further supported by its unambiguous synthesis[11] from dimethoxyresorcinol and bromoacetyl chloride.



I II

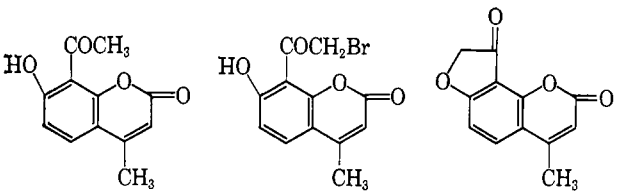


III IV

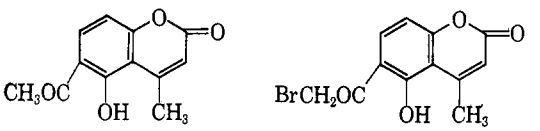


V

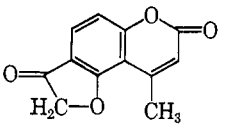
Similarly, 8-acetyl-7-hydroxy-4-methylcoumarin (VI) and 6-acetyl-5-hydroxy-4-methylcoumarin (VII) with cupric bromide in dioxane provided ω-bromo derivatives VIII and IX, respectively. VIII and IX gave the corresponding cyclic derivatives X and XI in alkaline medium.



VI VIII X



VII IX



XI

Bromination of 4-methylhydroxycoumarins with the usual brominating agents (as mentioned earlier) gave nuclear brominated products. The protection of hydroxyl group by acetylation leads to the formation of 4-bromomethyl derivatives with NBS[12] and the pyridine bromine complex.[13] However, cupric bromide in

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(3) A. W. Fort, *ibid.*, **26**, 765 (1961).
(4) E. R. Glazier, *ibid.*, **27**, 2937 (1962).
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(6) M. G. Marathey, *J. Sci. Ind. Res.* (India), **20B**, 40 (1961).
(7) B. J. Ghiya and M. G. Marathey, *ibid.*, **20B**, 41 (1961); **21B**, 28 (1962).
(8) P. N. Wadodkar, *Indian J. Chem.*, **1**, 122 (1963).
(9) (a) P. Friedlander and J. Neudoerfer, *Ber.*, **30**, 1077 (1897); (b) K. Auwers, *ibid.*, **45**, 975 (1912); **47**, 3307 (1914).
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(11) K. Auwers and P. Pohl, *Ann.*, **405**, 264 (1914).
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(13) B. J. Ghiya, Ph.D. thesis, Nagpur University, 1962.