Structure of Aryl Azo Pyrazolone Compounds and Their Copper Derivatives

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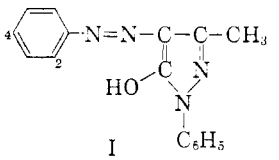
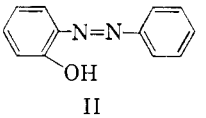
The simple aryl azo pyrazolone compounds (I) have been shown to be different from the simple *o*-hydroxy aryl azo compounds (II) in their



I



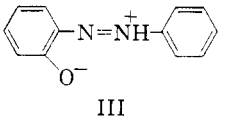
II

complexing ability with metal ions.[1] Although pyrazolone dyes are stronger acids, their metal derivatives are considerably more stable to dissociation into ions than the metal derivatives of type II. For example, the formation quotients of divalent copper, nickel, cobalt, and zinc with 1-phenyl-3-methyl-4-(4-methoxyphenylazo)-5-pyrazolone[2] are readily measured in 75 volume % dioxane-water while only the copper compound of 2-(4-methoxyphenylazo)-4-methyl-1-phenol[3] weakly forms under the same conditions.

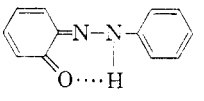
It has also been reported that there is only a small color shift in going from the undissociated dye, HCh, to the dissociated dye, Ch^-, of type (I)[1,2,4,5] while there is usually a significant color shift with type II, many of them serving as common indicators.

A preliminary infrared investigation of four simple aryl azo pyrazolone compounds, (Ia) 4-NO_2, (Ib) 4-OCH_3, (Ic) 2-OCH_3, and (Id) 2-SCH_3 and their copper(II) derivatives (2:1, dye to metal) shows no significant bands above 1700 cm.$^{-1}$ which are assignable to either the hydroxy or the NH group. However, a sharp, well defined band was found at 1670 cm.$^{-1}$ for dye (Ia), 1655 cm.$^{-1}$ for (Ib), and at 1665 cm.$^{-1}$ for (Ic) and (Id). This band disappeared completely in the copper derivatives.

Dolinsky and Jones[6] interpreted spectra of type II compounds as showing no evidence of either OH or of C=O absorption with the *o*-hydroxy compounds but that there was definite evidence in favor of the OH group with the *p*-hydroxy compounds. They proposed a zwitterion structure III as the most reasonable for the *o*-hydroxy (type II) derivatives. Recently Hadzi[7] interpreted his work with compounds of type II as arguing in favor of quinonehydrazone form (IV).



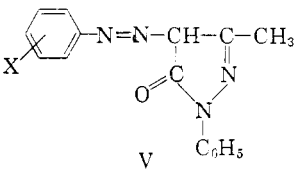
III



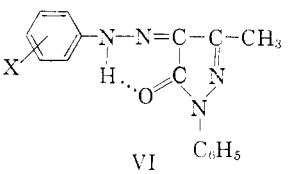
IV

Burawoy, *et al.*,[8] have used electronic spectra to show the existence of two distinct forms, the true hydroxy azo form II and the quinonehydrazone form IV.

We propose that either structure (V) or (VI) can represent the aryl azo pyrazolone compounds (the 1665 band is the carbonyl stretching band) and that (VII) represents the copper derivatives. The absence of significant absorption above 1700

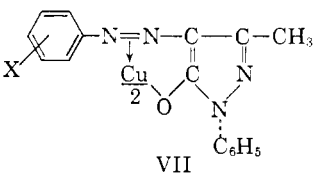


V



VI

cm.$^{-1}$ suggests that V is more reasonable than VI. However, as noted by Hadzi,[7] the band due to NH stretching would probably be broadened, weak, and shifted to longer wave lengths.



VII

EXPERIMENTAL

The azo compounds were prepared by coupling the appropriate diazotized amines to 1-phenyl-3-methyl-5-pyrazolone; they were recrystallized from dioxane. (Ia) 1-phenyl-3-methyl-4-(4-nitrophenylazo)-5-pyrazolone, red platelets, m.p. 199–200°, reported,[9] 198–199°; (Ib) 1-phenyl-3-methyl-4-(4-methoxyphenylazo)-5-pyrazolone, orange powder, m.p. 139–140°, reported[2] 139–140°; (Ic) 1-phenyl-3-methyl-4-(2-methoxyphenylazo)-5-pyrazolone, orange crystals, m.p. 166–167°, reported[2] 165–167°; (Id) 1-phenyl-3-methyl-4-(2-thiomethyoxyphenylazo)-5-pyrazolone, orange powder, m.p. 149–150°, reported[2] 149–150°. Each of the azo compounds was tested for purity, as previously reported.[4] Determination of neutral equivalents gave values within 0.1% of the calculated values.

The copper derivatives were prepared by the slow addition of 2 ml. of 1*N* NaOH solution to 100 ml. of boiling 75–25% dioxane-water which contained 2 mmoles of the dye and 1 mmole of copper(II) nitrate. The solutions were evaporated on a steam bath until precipitation of the com-

(1) F. A. Snavely and W. C. Fernelius, *Science*, **117**, 15 (1953).

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(3) C. G. Clark, Senior Honor Dissertation, Franklin and Marshall College (1957).

(4) F. A. Snavely, W. C. Fernelius, and B. P. Block, *J. Am. Chem. Soc.*, **79**, 1028 (1957).

(5) F. A. Snavely and B. D. Krecker, *J. Am. Chem. Soc.*, **81**, 4199 (1959).

(6) M. Dolinsky and J. H. Jones, *J. Assoc. Offic. Agr. Chemists*, **37**, 197 (1954).

(7) D. Hadzi, *J. Chem. Soc.*, 2143 (1956).

(8) A. Burawoy, *Ann.*, **509**, 60 (1934); A. Burawoy, A. G. Salem, and A. R. Thompson, *J. Chem. Soc.*, 4793 (1952).

(9) P. Karrer and E. B. Hershberg, *Helv. Chim. Acta*, **17**, 1014 (1934).

pound occurred. The metal derivatives were recrystallized from chlorobenzene, washed with ethyl ether, and dried in a vacuum desiccator. The copper derivative of (Ia), red-purple needles, m.p. 269–270°, reported[4] 268–270°.

The copper derivative of (Ib), brown crystalline powder, m.p. 237–238°.

Anal. Calcd. for Cu $(C_{17}H_{15}O_2N_4)_2$: C, 60.20; H, 4.46; N, 16.53. Found: C, 60.73; H, 4.29; N, 16.29.

The copper derivative of (Ic), brown crystalline powder, m.p. 286–287°, reported[10] 285°.

Anal. Calcd. for Cu $(C_{17}H_{15}O_2N_4)_2$: C, 60.20; H, 4.46; N, 16.53. Found: C, 60.67; H, 4.39; N, 16.28.

The copper derivative of (Id), brown powder, m.p. 233–234°.

Anal. Calcd. for Cu $(C_{17}H_{15}ON_4S)_2$: C, 57.48; H, 4.25; N, 15.77. Found: C, 57.37; H, 4.25; N, 15.43.

The spectra were measured, using the KBr disk technique on a Baird-Atomic two-beam infrared spectrophotometer.

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(10) V. I. Mur, *Zhur. Obshchei Khim.*, **24**, 572 (1954); *Chem. Abstr.*, **49**, 6198 (1955).

Some 4-Halo-2-butynyl *N*-Substituted Carbamates

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Many carbamates have been synthesized and screened for their biological activity as pesticides in the past few years. Although none are employed commercially as pesticides in this country at this time, certain acetylenic carbamates have been reported as having herbicidal activity.[1,2] Due to the fact that acetylenic compounds are rarely encountered in nature and that the carbamate linkage is known to be biologically active, the carbamates described herein were prepared and evaluated as pesticides. Several members of the series were found to be active, both as selective and as nonselective herbicides. The highly selective herbicidal activity of one of these compounds, 4-chloro-2-butynyl *N*-(3-chlorophenyl)carbamate, toward wild oats (*Avena fatua*) has been recently reported.[3] The variables regulating its use as a herbicide as well as the biological activities of the analogs in Table I will be reported elsewhere. No 4-chloro-2-butynyl *N*-substituted carbamate has been reported to have biological activity and only 4-chloro-2-butynyl *N*-phenylcarbamate, which is a member of this class of compounds, has been reported prior to this work.[4]

The compounds in Table I were prepared by four different methods:

(A) $ArN{=}C{=}O + HOCH_2C{\equiv}CCH_2X \longrightarrow ArNHCOOCH_2C{\equiv}CCH_2X$

(B) $RNH_2 + ClCOOCH_2C{\equiv}CCH_2X \longrightarrow RNHCOOCH_2C{\equiv}CCH_2X + HX$

(C) $ArN{=}C{=}O + HOCH_2C{\equiv}CCH_2OH \longrightarrow ArNHCOOCH_2C{\equiv}CCH_2OH$

$ArNHCOOCH_2C{\equiv}CCH_2OH + SOCl_2 \longrightarrow ArNHCOOCH_2C{\equiv}CCH_2Cl$

(D) $RNHCOOCH_2C{\equiv}CCH_2Cl + KI \longrightarrow RNHCOOCH_2C{\equiv}CCH_2I + KCl$

Method (C) has been used primarily for the preparation of 4-hydroxy-2-butynyl *N*-(3-chlorophenyl)carbamate. No solvent is necessary if the isocyanate addition is carried out above the melting point of the diol. The molar ratio of freshly distilled diol to isocyanate is important as regards the yield of the desired product. At a molar ratio of 1.25/1 the reaction mixture, when washed free of diol, contains 67% 4-hydroxy-2-butynyl *N*-(3-chlorophenyl)carbamate. At a molar ratio of 20/1 the yield of product in the reaction mixture is increased to 93%. The reaction mixtures were analyzed by their infrared absorption spectra, the band at 9.73μ being utilized to determine the concentration of the desired product.

The major impurity in the diol free reaction product would be expected to be 2-butynylene bis[*N*-(3-chlorophenyl)carbamate], which would be formed from the reaction of 4-hydroxy-2-butynyl *N*-(3-chlorophenyl)carbamate with isocyanate. The presence of the bis carbamate was confirmed by isolation from a reaction mixture. When an aliquot portion of the diol free reaction product was treated with excess isocyanate to convert the hydroxy carbamate to bis carbamate, only the bis carbamate was isolated.

The preparation of both the bromo and chloro halohydrins has been previously described by Bailey.[5] The chlorocarbonates were synthesized by the conventional reaction of phosgene with the halohydrin. These compounds were difficult to purify and were usually employed as the reaction mixture.

(1) J. A. Tursich, U. S. Patent **2,788,268** (1957).

(2) Badische Anilin, Ger. Patent **1,034,912** (1958).

(3) A paper entitled "Wild Oat Control with 4-Chloro-2-butynyl *N*-(3-Chlorophenyl)carbamate" by Otto L. Hoffmann, T. R. Hopkins, and Joe W. Pullen (in press) was presented at Winnipeg before the Proceedings of the 12th Annual Meeting, Western Section, National Weed Committee, Canada, on November 23, 1958 and before the North Central Weed Control Conference in Cincinnati on December 9, 1958. A paper entitled "Wild Oats—A New Chemical Control" by T. R. Hopkins, Otto L. Hoffmann, and Joe W. Pullen was presented before the Western Weed Conference at Salt Lake City on March 19, 1959.

(4) G. Dupont, R. Dulon, and G. Lefebure, *Bull. soc. chim. France*, 816 (1954).

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