

Anal. Subs., 0.1390: CO₂, 0.3022; H₂O, 0.0781. Calc. for C₁₅H₁₃O₄N₃: C, 59.01; H, 6.22. Found: C, 59.29; H, 6.24.

The fourth product, the semicarbazone of α -semicarbazido-ethyl-*p*-ethoxy-benzoylacrylate, was always obtained in the reaction with the yellow ethyl ester when the solid (154°) remained in solution in the quantity of alcohol used and could be separated by taking advantage of the fact that it is not soluble in acetone.

Semicarbazone of *p*-Ethoxy-benzoylacrylic Acid, C₂H₅OC₆H₄CCH=CHCOOH.—

$$\begin{array}{c} \parallel \\ \text{NNHCONH}_2 \end{array}$$

The semicarbazone of the unsaturated acid was prepared by treating a methyl alcohol solution of the acid with semicarbazide. After the mixture had stood for two hours, the product was filtered off, washed with water and methyl alcohol and dried. It melted at 212° with decomposition.

Anal. Subs., 0.1503: CO₂, 0.3107; H₂O, 0.0751. Calc. for C₁₃H₁₅O₄N₃: C, 56.31; H, 5.41. Found: C, 56.37; H, 5.55.

Summary

The yellow methyl and ethyl esters of *p*-ethoxy-benzoylacrylic acid isomerize when exposed to the sunlight both as solids and in benzene solution. The unstable, colorless esters thus formed are transformed quantitatively, both in the dark and in the sunlight when in benzene solutions containing a crystal of iodine, into the stable yellow isomers. Hydrochloric acid brings about the same change.

Hydrolysis of the esters has been studied. With semicarbazide the colorless isomers form addition products and semicarbazones of these addition products. The yellow isomers give in addition to these, two substances, namely, the isomeric semicarbazones; *p*-ethoxy-benzoylacrylic acid forms a semicarbazone. The behavior of the ethoxy compounds is like that of the corresponding methoxy compounds and different from that of benzoylacrylic acid and its esters.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

SOME REDUCTION PRODUCTS OF 1-NITRO- AND 3-NITROCARBAZOLE

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It has been shown¹ that when carbazole is nitrated, using acetic acid as the solvent and keeping the temperature of the mixture at 80°, two mononitro compounds are formed; both are easily reduced to the corresponding amino compounds. Also the two nitro compounds can be easily separated due to their different solubilities in acetic acid, the 3-nitrocarbazole being relatively insoluble, while the 1-nitrocarbazole is much more soluble in this solvent. While this is the first mention of the 1-amino compound, the 3-amino derivative had previously been made from

¹ Ziersch, *Ber.*, **42**, 3797 (1909).

the N-nitroso-3-nitrocarbazole by the reduction with stannous chloride.² Since the nitro group is so easily reduced to the amino group and no attempts have been made to synthesize any of the intermediate reduction products, except the 3-nitrosocarbazole mentioned in the literature,³ it was thought that it would be of interest to prepare some of these products, or attempt their preparation.

In studying the effects of different reducing agents on these two nitro compounds the first effect noticed was the ease with which the nitro group is reduced. When heated with alcoholic sodium or potassium hydroxide both of the nitro compounds are reduced to the corresponding azoxy products. The azoxy compounds when dissolved in alcohol and treated with zinc dust are easily reduced to the azo derivatives. When attempts were made to obtain the hydrazo compounds by reducing the azoxy-, azo-, or nitrocarbazole with zinc dust and alcoholic potassium hydroxide the corresponding amino compounds were obtained.

The amino compound can be obtained by the reduction of the nitrocarbazole with zinc dust and hydrochloric acid in an alcoholic solution. The amine and the zinc chloride can be separated by pouring the alcohol solution into water and adding an excess of ammonia. The amine remains as a precipitate and the zinc dissolves. The crude product is recrystallized from alcohol. This is a very much quicker method than the reduction with stannous salts and the subsequent separation of the amine and the tin salts by means of hydrogen sulfide.

Experimental Part

Nitration.—Ziersch¹ has recommended that the nitration take place at 80°; in this work it was found that better results were obtained when the mixture of carbazole and acetic acid, 1 g. of the carbazole to 80 cc. of the acid, was heated only to 60° and then the nitric acid dropped in slowly. The heat generated by the reaction was sufficient to cause quite a rise in temperature, and sometimes it was necessary to cool the mixture to prevent the temperature from rising above 80°. The product thus obtained was usually much freer from resinous impurities.

As the mixture cooled the 3-nitrocarbazole separated, leaving the 1-nitrocarbazole in solution. The precipitate was filtered off, washed with a little acetic acid and dried. The 1-nitrocarbazole was obtained by pouring the filtrate into water. The products thus obtained were usually pure enough to be used in the preparation of other derivatives. Recrystallizing the 3-nitrocarbazole from acetic acid yields yellow crystals, m. p., 205°, while recrystallizing the 1-nitrocarbazole from alcohol yields light yellow crystals; m. p., 164°.

3-Azoxycarbazole, $\text{NC}_{12}\text{H}_8\text{NONC}_{12}\text{H}_8\text{N}$.—The 3-azoxycarbazole is obtained when 3 g. of the 3-nitrocarbazole is added to 50 cc. of alcohol and to this mixture is added 3 g.

² Ruff and Stein, *Ber.*, **34**, 1679 (1907).

³ Schott, Ger. pat., 134,983; *Chem. Zentr.*, 1902, II, 1165.

of sodium hydroxide dissolved in about 10 cc. of water. The final mixture is heated gently until all of the nitro compound is dissolved; in the presence of the alkali this takes place rapidly with the formation of an intensely red solution. The liquid is then heated to boiling and refluxed for three to four hours. At the end of this time it is poured into water, the yellow precipitate formed is washed well with water by decantation, filtered off, and recrystallized from alcohol. The 3-azoxycarbazole forms as light yellow crystals; m. p., 208–209°; yield, about 80%.

Anal. Calc. for $C_{24}H_{16}ON_4$: N, 14.89. Found: 14.70.

1-Azoxycarbazole.—This compound can be prepared in exactly the same manner from the 1-nitrocarbazole, except that after precipitating with water and filtering it is necessary to extract with alcohol using an extraction tube. With this compound there appears to be formed a large amount of resinous material, some of which is insoluble in alcohol. From the alcohol solution the 1-azoxycarbazole is obtained as light yellow crystals; m. p., 183–185°; yield, about 70%.

Anal. Calc. for $C_{24}H_{16}ON_4$: N, 14.89. Found: 14.44.

3-Azocarbazole, $NC_{12}H_8N$ — $NC_{12}H_8N$.—The 3-azocarbazole is obtained when the 3-azoxycarbazole is dissolved in alcohol and the boiling solution treated with zinc dust in small portions. The weight of zinc dust required is about two and a half to three times the weight of azoxycarbazole used and best yields were obtained by refluxing for at least three hours. The alcoholic solution is filtered from the zinc dust, and the 3-azocarbazole allowed to crystallize from solution. Large, coarse, red crystals, m. p. 215°, were obtained; yield, about 80%.

Anal. Calc. for $C_{24}H_{16}N_4$: N, 15.54. Found: 15.15.

1-Azocarbazole.—This is obtained similarly from the 1-azoxycarbazole, and crystallizes in light, fine, reddish-brown crystals; m. p., 196–197°; yield, about 80%.

Anal. Calc. for $C_{24}H_{16}N_4$: N, 15.54. Found: 15.27.

1-Aminocarbazole, $NC_{12}H_8NH_2$.—This compound was obtained when the nitro-, azo-, or the azoxycarbazole was dissolved in alcoholic potassium hydroxide and then reduced with zinc dust. It was hoped that instead of this compound the corresponding hydrazo compound would be formed. Best results were obtained when equal weights of any one of the compounds mentioned and potassium hydroxide were dissolved in alcohol, using 50 cc. of alcohol for every gram of substance to be reduced and adding the zinc dust in small portions to the boiling solution. When the solution became colorless the alcohol was filtered from the zinc, poured into water, the amine precipitating was filtered off and crystallized; m. p., 226–228°. The yield varied with the substance reduced, but was usually about 50–60%.

The ACETYL DERIVATIVE was made by dissolving the amine in acetic acid, adding to the solution an excess of acetic anhydride and allowing the mixture to stand for two to three hours. The mixture was poured into water, the acetyl compound which precipitated was filtered off and crystallized from alcohol; m. p., 170–171°; yield, about 50%.

Anal. Calc. for $C_{12}H_9N_2 \cdot C_2H_3O$: N, 12.50. Found: 12.14.

3-Aminocarbazole.—This compound was obtained when the corresponding nitro-, azoxy-, or azocarbazole was reduced as described above, using alcoholic potassium hydroxide and zinc dust. When crystallized from alcohol the white crystals obtained by the reduction of the 3-nitrocarbazole melted at 254°; this melting point agrees with that given by Ruff and Stein.² The crystals obtained from the reduction of the azo and azoxy carbazole melted at 247–248°, which agrees with the melting point given by Ullmann.⁴ Just why these differences should exist is difficult to say.

⁴ Ullmann, *Ber.*, **31**, 1697 (1889).

The ACETYL DERIVATIVE can be made as already described, dissolving the amine in acetic acid and adding acetic anhydride. This compound melts at 214°, and is obtained from either of the two 3-nitrocarbazoles just mentioned.

The acetyl derivative when dissolved in acetic acid and treated with either sodium or potassium nitrite yields the N-nitroso compound which when crystallized from alcohol melts with decomposition at 162–164°.

Both of these last mentioned compounds had been previously made by Mazzara and Leonardi,⁵ though in making the acetyl derivative they heated the mixture of amine and acetic anhydride, while in this work the reaction was found to proceed fairly rapidly in the cold. These two compounds were also made in order to establish the fact that when either nitrocarbazole or one of the intermediate reduction products was reduced in an alkaline solution with zinc dust the amino and not the hydrazo compound was obtained.

Summary

1. From 1-nitro- and 3-nitrocarbazole the corresponding azoxy and azo compounds have been prepared.

2. It has been shown that in an alkaline solution both the 1-nitro- and 3-nitrocarbazole, as well as the corresponding azoxy and azo compounds, are reduced to the amine.

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THE EFFECT OF SULFUR ON THE COLOR OF TRIPHENYLMETHANE DYES

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Introductory and Historical

Within the last several years, a considerable amount of work has been done in this Laboratory on the auxochrome effect of alkyl-linked sulfur, more particularly in the field of azo dyes.^{1a}

The present investigation is a further extension of this idea into the field of triphenylmethane dyes. A search through the literature showed few triphenylmethane dyes containing alkyl-linked sulfur.

Brand and Stallmann² have studied the auxochrome effect of alkyl mercapto groups on the phenol ethers of triphenylmethane. They have prepared compounds of the type $(C_6H_5)_2C(OH)C_6H_4SCH_3$ (*o*) and $C_6H_5C(HO)(C_6H_4SCH_3)_2$ (*o*) and have shown that such compounds in acetic acid or alcoholic solution when treated with strong sulfuric or hydrochloric acid, develop color. These cannot be classed as true dyes although they do show the auxochrome effect of the $-SCH_3$ group.

⁵ Mazzara and Leonardi, *Gazz. chim. ital.*, [2] 21, 385 (1891).

¹ From the Doctor's dissertation of H. S. Holt, 1924.

^{1a} (b) Waldron and Reid, *THIS JOURNAL*, 45, 2399 (1923). (c) Foster and Reid, *ibid.*, 46, 1936 (1924).

² Brand and Stallmann, *Ber.*, 54, 1578 (1921).