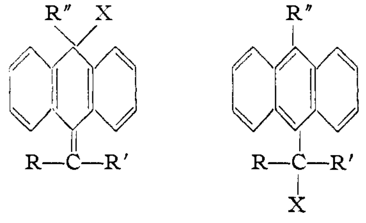
[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE GLIDDEN COMPANY, SOYA PRODUCTS DIVISION]

Conjugated Systems. VII. A Resonance Hybrid to which a Triarylmethyl and a Biarylnitrogen are Contributing Structures

BY PERCY L. JULIAN, WAYNE COLE AND RALPH SCHROEDER

In the preceding communication[1] and an earlier one[2] a somewhat exhaustive study of the mobile tautomeric system represented by structures (I) and (II) has been reported. Although certain evidence for an equilibrium between the two structures has been adduced, it appears that structure II is the more stable and more frequently occurring in the syntheses of these isomers, and we have suggested that the driving force in the interconversions is the tendency to form the more stable aromatic structure of anthracene.



(I) (II)

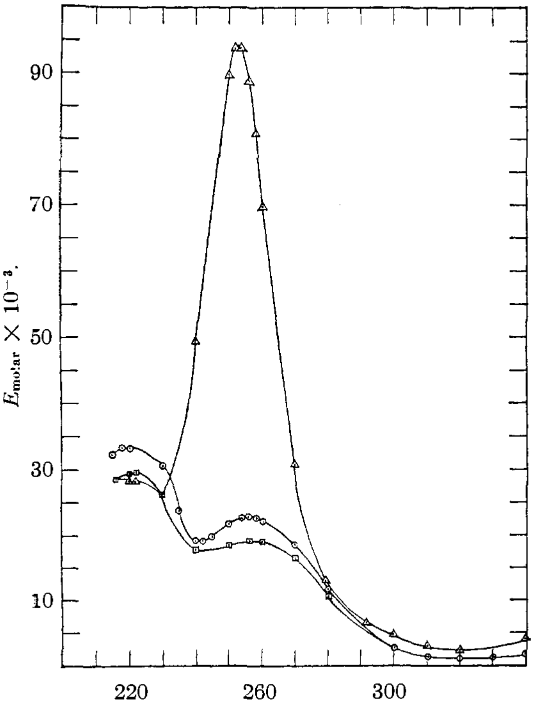


Fig. 1.—Molecular extinction coefficients: —O—O—, 9-phenyl-9-hydroxy-10-anilo-9,10-dihydroanthracene (IV); —□—□—, 9-phenyl-9-chloro-10-anilo-9,10-dihydroanthracene (VII); —△—△—, 9-phenyl-10-anilinoanthracene (XII).

In the present investigation we were interested at the outset in knowing how a free radical would behave which resulted from removal of X in formula I above. A more fortunate selection for the first study of a free radical of this general structure would seem to reside in the removal of halogen from the tertiary halide (VII). For the resulting resonance hybrid, represented schematically by bracketed formulas (IX), (X), etc., would be a free radical to which two of the contributing structures would be a triarylmethyl (IX) and a biarylnitrogen (X). In view of our previous experiences, we would expect derivatives of this free radical, such as, for example, the nitric oxide adduct, to possess what we have called the more stable anthracene structure XIII. This paper reports the experimental realization of these predictions.

10-Anilo-9-anthrone (III)[3] on treatment with phenylmagnesium bromide gave 10-anilo-9-phenyl-9-hydroxy-9,10-dihydroanthracene (IV). Attempts to convert it into the corresponding tertiary chloride (VII) served likewise to give proof of its structure. Dry hydrogen chloride in ether gave a crystalline hydrochloride (V) which on refluxing with ethyl alcohol yielded phenyloxanthrone (VI). On treatment of the carbinol (IV) with thionyl chloride in pyridine, 10-anilo-9-phenyl-9-chloro-9,10-dihydroanthracene (VII) was obtained as a highly unstable substance which had to be used immediately. On treating it with ethyl alcohol, it was converted quantitatively into 9-phenyl-9-ethoxy-10-anthrone (VIII)[4] and aniline hydrochloride. Sodium methoxide converted the chloro-compound (VII) into 9-phenyl-9-methoxy-10-anilo-9,10-dihydroanthracene (XI). Moreover, Fig. 1 shows the ultraviolet absorption spectra of the tertiary halide (VII), and of its parent carbinol (IV), to be different from that of a typical anthracene analog (XII). The constitution of the tertiary halide (VII) is, therefore, established.

On shaking an ethereal solution of the tertiary chloride (VII) with molecular silver or copper bronze a pronounced cherry-red color developed, indicative of the presence of a free radical. Efforts to trap this free radical in the form of a peroxide were unsuccessful. On passing oxygen into the solution of VII while shaking with copper bronze or molecular silver, the red color rapidly disappeared and the solution took on a greenish-yellow fluorescence; however, the product iso-

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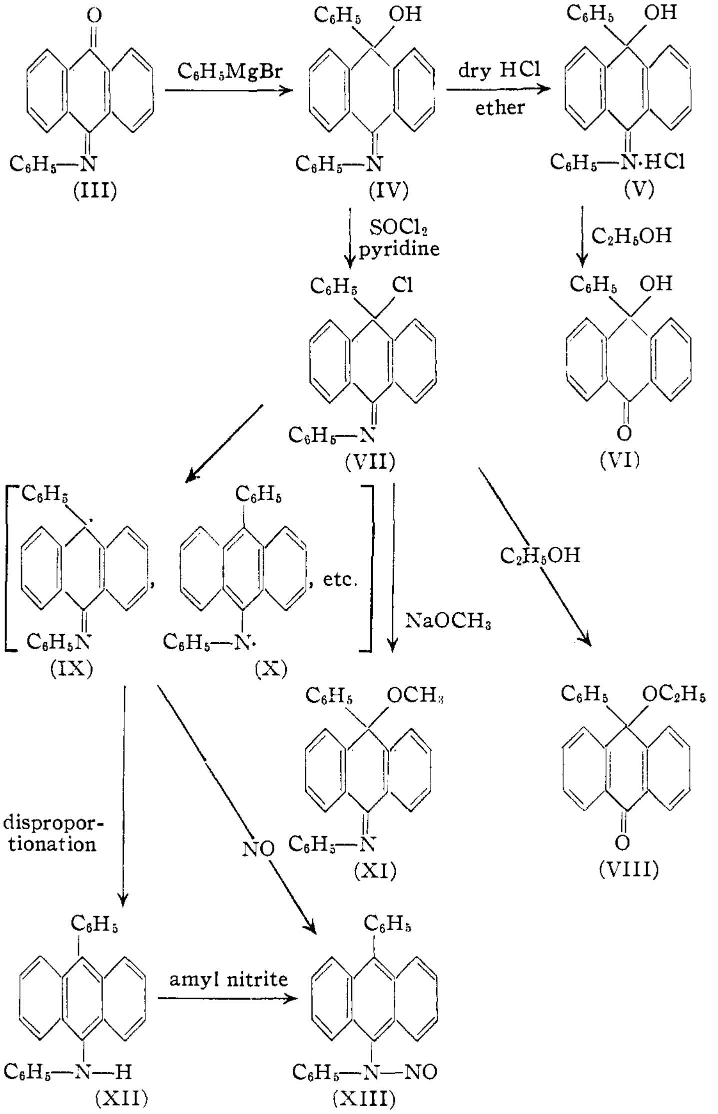
[1] Paper VI of this series. Julian, Cole, Diemer and Schafer, THIS JOURNAL, **70**, 2058 (1948).

[2] Julian and Cole, *ibid.*, **57**, 1607 (1935).

[3] Meyer and Sander, *Ann.*, **396**, 145 (1913).

[4] Liebermann and Linderbaum, *Ber.*, **38**, 1802 (1905).



lated was the same as that obtained when the free radical was prepared in an atmosphere of nitrogen, namely, 10-anilino-9-phenylanthracene (XII), a disproportionation product of the biarylnitrogen structure (X).[5,6]

Although neither the hydrazyl (X) nor its bimolecular modification, the tetraarylhydrazine, could be isolated, conclusive evidence for the formation of the nitrogen free radical (X) resides in isolation of its nitric oxide addition product, obtained by passing pure nitric oxide into the ethereal solution of VII while shaking with molecular silver or copper bronze. Synthesis of this adduct from XII with amyl nitrite showed it to be 10-N-nitrosoanilino-9-phenylanthracene (XIII). The remaining product or products of the disproportionation of the free radical (X), other than XII, could only be obtained in the form of intractable gums.

The real significance of the free radical preparation described in this communication resides in the fact that it is the first instance of the direct formation of a biarylnitrogen in its monomeric state. Indeed, except for the radical α,α-diphenyl-β-trinitrophenylhydrazyl,[7] it constitutes the only preparation of a "nitrogen free radical" that did not depend upon the dissociation of a fairly stable hydrazine or tetrazane.[6,8]

From the observations of Wieland,[6] one might have predicted a most rapid disproportionation of such a biarylnitrogen as structure (X). This author showed, for example, that the greater the tendency toward dissociation of a tetraarylhydrazine into its corresponding biarylnitrogen, the more rapid was its destruction by disproportionation. Thus the readily dissociable *p*-tetraanisylhydrazine was destroyed (by disproportionation) most rapidly in the solvent in which its dissociation was highest.

Experimental

10-Anilo-9-phenyl-9-hydroxy-9,10-dihydroanthracene (IV).—To a solution of Grignard reagent made fom 0.057 mole of bromobenzene (9.0 g.) and 0.062 mole of magnesium (1.5 g.) a solution of 0.028 mole of anthrone anil (8.0 g.) in anhydrous ether–benzene mixture was added slowly over a twenty-minute period with stirring at room temperature. The reaction was continued for one hour after addition was complete, following which it was decomposed with ammonium chloride in ice-water. The product was extracted with ether and washed with water; the ether extract was then concentrated and crystallized by the slow addition of petroleum ether; yield 8.7 g., 85%; m. p. 165°.

Anal. Calcd. for $C_{26}H_{19}ON$: C, 86.40; H, 5.30. Found: C, 86.65; H, 5.37.

By dissolving (IV) in dry ether and passing in dry hydrogen chloride, a yellow precipitate of the hydrochloride begins to form immediately. This compound when filtered proves to be somewhat unstable, becoming gummy after it stands for a short time. When freshly prepared, the m. p. is 135° with decomposition. Refluxing with wet alcohol and subsequent crystallization yields phenyloxanthrone (VI), m. p. 213–214°.

10-Anilo-9-phenyl-9-chloro-9,10-dihydroanthracene (VII).—To a solution of 900 mg. of (IV) in 50 cc. of anhydrous ether containing 200 mg. of pyridine, a solution of 600 mg. of thionyl chloride in 10 cc. of anhydrous ether was added while shaking. A precipitate of pyridine hydrochloride formed immediately and was filtered off after allowing the reaction to stand for fifteen minutes. The ether solution was quickly washed two times with water, dried over sodium sulfate and taken to dryness under vacuum without heat. A non-crystalline orange gum resulted which was quite unstable, turning black on short exposure to air, or in solution gradually forming condensa-

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(5) *Cf.* Wieland, *Ann.*, **392**, 158 (1912).

(6) *Ber.* **48**, 1078 (1915).

(7) Goldschmidt and Renn, *Ber.*, **55**, 628 (1922).

(8) Goldschmidt, *ibid.*, **53**, 28, 44 (1920); **55**, 616 628, 644 (1922).

tion products. The gum is soluble in all common solvents, particularly so in chlorinated solvents.

Anal. Calcd. for $C_{26}H_{18}NCl$: N, 3.71; Cl, 9.33. Found: N, 3.5; Cl, 9.7.

When the non-crystalline orange gum (VII) is heated with ethyl alcohol the anilo group is cleaved by hydrogen chloride formed in the reaction and 10-oxo-9-phenyl-9-ethoxy-9,10-dihydroanthracene (VIII) is formed; m. p. 155–156°. This agrees with the melting point recorded in the literature[9] and gives no depression when mix melted with a reference sample.

When (VII), freshly prepared from 3.6 g. of (IV) and the ether solution dried and concentrated to about 25 cc., was added to a solution of 2 g. of dry sodium methoxide in dry benzene and the reaction shaken for seventeen hours, a precipitate of salt could be seen. After washing the solution with water, drying and concentrating, crystallization was effected with the addition of petroleum ether. Bright orange rosettes of 10-anilo-9-phenyl-9-methoxy-9,10-dihydroanthracene (XI) were obtained in 90% yield; m. p. 132–134°.

Anal. Calcd. for $C_{27}H_{21}ON$: C, 86.37; H, 5.64. Found: C, 86.10; H, 5.55.

When (XI) is refluxed in 1% solution of hydrogen chloride in wet methanol, the anilo group is cleaved to give 10-keto-9-phenyl-9-methoxy-9,10-dihydroanthracene, m. p. 169–171°, identical with the compound prepared by Haller and Guyot.[10]

Free Radical Formation by Shaking with Copper Bronze.—A freshly prepared ether solution of (VII) made from 3.6 g. of (IV) was dried as quickly as possible by freezing out water, then drying over sodium sulfate. The ether solution thus obtained was shaken with 4 g. of copper bronze under an atmosphere of nitrogen for a period of four hours. The initial light orange-colored solution quickly deepened in color after shaking began and at the end of fifteen minutes was deep cherry-red; a yellowish-green precipitate meanwhile deposited slowly on the sides of the flask. The red coloration was gradually lost until at the end of about three hours it was no longer evident.

By concentrating the ether solution almost to dryness a residue was obtained which was extracted with benzene and filtered to remove copper bronze. On concentrating the benzene solution, 48% of the material crystallized in yellowish-green needles melting, when purified, at 224°. These proved to be 10-anilino-9-phenylanthracene (XII).

Anal. Calcd. for $C_{26}H_{19}N$: C, 90.40; H, 5.54; N, 4.06; mol. wt., 345.4. Found: C, 90.11; H, 5.34; N, 3.96; mol. wt. (Rast), 347.

Comparison of this compound was made with 10-anilino-9-phenylanthracene prepared by condensing 9-phenylanthrone with aniline similar to Padova's preparation[11] of 10-anilinoanthracene. They proved to have the same melting point and give no depression when mixed.

After crystallization of (XII) the mother liquor yielded no further crystalline product, only an orange gum resulting on concentration.

By repeating the experiment under an atmosphere of oxygen rather than nitrogen, no reddening of the solution could be perceived as it was shaken with copper bronze. End products of the reaction, however, were the same, and in the same yield.

10-N-Nitrosoanilino-9-phenylanthracene (XIII).—By carrying out the reaction of (VII) with copper bronze under an atmosphere of nitric oxide,[12] the red coloration which initially took place was quickly dispelled. The product obtained was 10-N-nitrosoanilino-9-phenylanthracene (XIII), m. p. 174–175°.

Anal. Calcd. for $C_{26}H_{18}N_2O$: C, 83.40; H, 4.85; N, 7.48. Found: C, 83.11; H, 4.94; N, 7.23.

Preparation of (XIII) was carried out in a manner analogous to the preparation of N-nitrosodiphenylamine[13] by treating 10-anilino-9-phenylanthracene with butyl nitrite. This gave a compound melting at 173–174° and showing no depression in melting point when mixed with a sample of the nitric oxide adduct of the free radical (X).

Summary

The removal of chlorine from 9-phenyl-9-chloro-10-anilo-9,10-dihydroanthracene with copper bronze or molecular silver results in formation of a resonance hybrid radical, one of the contributing structures to which is the biarylnitrogen, 10-(9-phenylanthracyl)-phenylnitrogen.

This new biarylnitrogen disproportionates rapidly and one of the disproportionation products, namely, 10-anilino-9-phenylanthracene, was isolated and identified. The nitric oxide adduct of the free nitrogen radical was also prepared.

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[9] Liebermann, *Ber.*, **38**, 1802 (1905).

[10] Haller and Guyot, *Bull. soc. chim.*, [3] **17**, 877 (1897).

[11] Padova, *Compt. rend.*, **149**, 218 (1908).

[12] W. A. Noyes, THIS JOURNAL, **47**, 2170 (1920).

[13] E. Fischer, *Ann.*, **190**, 174 (1886).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

The Synthesis of 1,4-Dibenzoyl-1,3-butadiene[1,2]

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Long conjugated systems of the 1,4-dibenzoyl-1,3-butadiene type are of interest because of the varied possibilities of reaction. In this paper is described the synthesis of 1,4-dibenzoyl-1,3-butadiene (II), itself, from muconic acid (I) by means of the Friedel–Crafts reaction between muconyl chloride and benzene. Since the muconic acid was the *trans–trans* isomer,[3] the dibenzoylbutadiene made from it should have the *trans–trans* configuration.[4]

The reaction leading to II furnishes evidence as to its structure. Further proof was obtained by reduction and by reaction with diazomethane. Catalytic reduction yielded known 1,4-dibenzoylbutane (V); whereas reduction with zinc and acetic acid gave a substance formulated as IV because of its resistance to further reduction by this reagent. The butene (IV) would be expected to be stable to reduction by means of metal combinations, since a conjugated system is no

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[1] A portion of this work was taken from the M.A. thesis of J. H. Ross, May, 1948.

[2] This work was supported in part by grants from the University Research Institute, Project 70, and from the Research Corporation, New York, N. Y.

[3] Behrend, *Ber.*, **49**, 999 (1916); Behrend and Heyer, *Ann.*, **418**, 294 (1919).

[4] *Cf.* the synthesis of *trans*-1,2-dibenzoylethylene from fumaryl chloride, Conant and Lutz, THIS JOURNAL, **45**, 1303 (1923).