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).

CHICAGO, ILLINOIS RECEIVED AUGUST 2, 1948

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

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

BY PHILIP S. BAILEY AND JOSEPH H. ROSS

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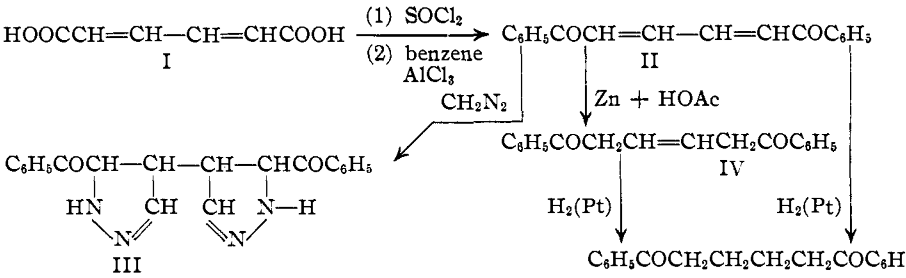
[1] A portion of this work was taken from the M.A. thesis of J. H. Ross, May, 1948.

[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.

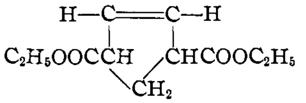
[3] Behrend, *Ber.*, **49**, 999 (1916); Behrend and Heyer, *Ann.*, **418**, 294 (1919).

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



longer present.[5] Catalytic reduction of IV gave V.

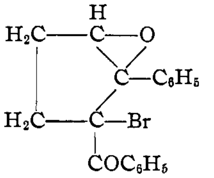
When dibenzoylbutadiene (II) was treated with diazomethane it was found that two molecules of diazomethane reacted with one molecule of II to give a yellow substance formulated as III, by analogy to the reactions of other α,β-unsaturated ketones[6] and esters[5,6] with diazomethane. It is interesting to note that diazomethane has been found to react with the diethyl ester of muconic acid by a 1,4-reaction rather than a 1,2-reaction to give a cyclopentene derivative (VI) instead of the usual pyrazoline derivative such as III.[7]



VI

Light has been found to have an effect upon dibenzoylbutadiene (II). When exposed to sunlight in or out of solution, the yellow II is converted to a colorless substance with a higher melting point. Its percentage composition and molecular weight indicate it to be a dimer of II. It shows both carbon–carbon and carbon-oxygen unsaturation. Since it was thought possible for the substance to be a Diels–Alder addend in which dibenzoylbutadiene acted both as a diene and a dieneophile, attempts were made to carry out a Diels–Alder reaction between two molecules of dibenzoylbutadiene under more usual conditions. When dibenzoylbutadiene was heated at its melting point for several minutes, decomposition occurred. The dimer likewise decomposed under similar conditions. Heating ethanol, *t*-butyl alcohol, benzene, xylene or nitrobenzene solutions of II at the reflux temperature for various periods of time either gave no reaction or caused decomposition. A further study of the structure of the dimer will be made and reported at a later date. Other reactions of dibenzoylbutadiene (II) also seem to be of a more complicated nature and will be reported in later publications.

Attempts to prepare dibenzoylbutadiene (II) by the dehydrohalogenation of 1,4-dibenzoyl-1,4-dibromobutane failed. When a large excess of potassium hydroxide in methanol or ethanol solution was used, or when a suspension of the dibromo compound in triethylamine was refluxed long enough for reaction to occur, only tars and resins were obtained. When the reaction was carried out using a ratio of five moles of potassium hydroxide to one mole of the dibromo compound in either methanol or ethanol solution, a compound (VII) reported earlier by Fuson and coworkers[8,9] and by Kao[10] was obtained. It was reduced by zinc and acetic acid to give 1,4-dibenzoylbutane in low yield, a reaction reported earlier to take place with the corresponding chloro compound.[9]



VII

Experimental[11]

Muconyl chloride was made by heating at reflux temperature a mixture of 14.2 g. of muconic acid[12] and 90 ml. of thionyl chloride for forty-five hours, during which time solution occurred. The excess thionyl chloride was removed by vacuum distillation over a steam-bath. On cooling, the residue crystallized. It was used in the synthesis of dibenzoylbutadiene without further purification.

1,4-Dibenzoyl-1,3-butadiene (II).—To a well-stirred mixture of 185 ml. of dry benzene and 30 g. of anhydrous aluminum chloride, heated to 50–60°, was added a solution of the crude muconyl chloride, prepared above, in about 25 ml. of benzene. The addition was carried out as fast as possible depending on the extent of frothing, after which, heating was continued with stirring for an additional ten minutes. The black reaction mixture was poured onto ice and water containing 20 ml. of concd. hydrochloric acid. A yellow solid separated and was dissolved by treatment with 400 ml. of warm benzene. The benzene layer was separated and thoroughly washed and cooled. Filtration yielded 23.3 g. (89% yield) of yellow crystals melting at 177–184°. Several recrystallizations from ethanol and from benzene raised the melting point to 193–195°. The compound readily decolorized an acetone solution of potassium permanganate.

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[5] Allen and Blatt in Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 666-700.

[6] Richter and Anschütz, "The Chemistry of the Carbon Compounds," Vol. IV (Eng. Trans.), Elsevier Publishing Co., New York, N. Y., 1947, p. 102.

[7] Guha and Sankaran, *Ber.*, **70**, 2109 (1937).

[8] Kao and Fuson, This Journal, **54**, 313 (1932).

[9] Fuson, Hully, McPherson and Spangler, *J. Org. Chem.*, **7**, 462 (1942).

[10] Kao, This Journal, **62**, 356 (1940).

[11] The melting points reported here are corrected. Some of the microanalyses were done by the Micro-Tech Laboratories of Skokie, Illinois, and the Clark Microanalytical Laboratories of Urbana, Illinois.

[12] Prepared by the method of Guha and Sankaran, in Adkins, "Organic Syntheses," Vol. 26, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 57.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.17; H, 5.44.

Reduction of 1,4-Dibenzoyl-1,3-butadiene (II). (a) To 1,4-Dibenzoylbutane (V).—A solution of 0.46 g. of dibenzoylbutadiene (II) in 50 ml. of benzene was allowed to absorb hydrogen in the presence of platinum oxide catalyst (0.1 g.). The reaction was stopped after 2.4 mole equivalents had been absorbed, at which point the rate had decreased greatly. Filtration and evaporation yielded a solid residue which upon recrystallization from benzene melted at 106–108° and was shown to be 1,4-dibenzoylbutane by a mixture melting point with an authentic sample.[13]

(b) To 1,4-Dibenzoyl-2-butene (IV)—Six grams of zinc dust was added to a solution of 5 g. of dibenzoylbutadiene (II) in 100 ml. of hot glacial acetic acid. The mixture was heated over the steam-bath for fifteen minutes, after which it was filtered and the filtrate was poured into water. A pasty solid separated and was filtered off and washed. It weighed 2.8 g. and melted at 118–133°. Several recrystallizations from benzene and from carbon tetrachloride raised the melting point to 135–136.6°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.55; H, 5.93.

Reduction of 1,4-Dibenzoyl-2-butene (IV).—A mixture consisting of a benzene solution of 0.57 g. of IV and 0.23 g. of platinum oxide was allowed to absorb hydrogen at room temperature and pressure. After the rate of absorption had decreased, the reaction mixture was filtered and the filtrate was evaporated. Crystallization and recrystallization of the residue from carbon tetrachloride yielded dibenzoylbutane (V); m. p. 106–108°, identified by the mixture melting point method.

Reaction of 1,4-Dibenzoyl-1,3-butadiene (II) with Diazomethane to give 4,4′-bis-(5-Benzoylpyrazoline) (III).—To 165 ml. of an ether solution of diazomethane, prepared from 16.5 g. of nitrosomethylurea, was added 6 g. of dibenzoylbutadiene (II) and a small amount of benzene. After standing overnight the reaction mixture was filtered; 4.3 g. of yellow crystals decomposing at 176–205° was obtained. Several recrystallizations from benzene and from ethanol (large volumes required) raised the decomposition point to 213–218°.

Anal. Calcd. for $C_{20}H_{18}N_4O_2$: C, 69.35; H, 5.24; N, 16.18. Found: C, 69.27; H, 5.40; N, 16.02.

Reaction of 1,4-Dibenzoyl-1,3-butadiene (II) in Sunlight.—A mixture of 10 g. of crude II suspended in ethanol and benzene was allowed to stand in bright sunlight for about twenty-five hours. Evaporation and recrystallization of the residue from 100 ml. of ethanol yielded 4.5 g. of colorless crystals which melted at 175–191°. Several recrystallizations from benzene and from ethanol raised the melting point to 207–208°. The change from II to the colorless compound was also noticed when the dry material was exposed to sunlight. The compound was usually encountered also when working up the reaction mixture from the preparation of dibenzoylbutadiene unless all work was done at night.

Anal. Calcd. for $C_{36}H_{28}O_4$: C, 82.42; H, 5.38; mol. wt., 524. Found: C, 82.02, 82.01; H, 5.41, 5.40; mol. wt. (Rast), 532, 537, 520.

The compound readily decolorized an acetone solution of potassium permanganate. It reacted with hydroxylamine in pyridine–alcohol solution after two hours reflux. The product melted at 241–244°; it could not be purified for analysis, however, since it was insoluble in most solvents. It decomposed when attempts were made to recrystallize it from dioxane in which it was somewhat soluble. Attempts to reduce the dimer catalytically (platinum) or with zinc and acetic acid gave resinous materials. When the dimer was heated at its melting point until it turned orange, no change in composition occurred, but when it was heated longer, decomposition to a tar took place.

Attempted Diels–Alder Reaction between Two Molecules, of 1,4-Dibenzoyl-1,3-butadiene (II).—Benzene, ethanol and *t*-butyl alcohol solutions of II were refluxed for fifty to eighty hours. When the solutions were cooled, crystallization occurred and good recoveries of dibenzoylbutadiene were obtained. When xylene and nitrobenzene solutions of II were refluxed for thirty-five and twenty-five hours, respectively, the solutions became dark and nothing crystalline could be obtained from them.

The Action of Alcoholic Potassium Hydroxide on 1,4-Dibenzoyl-1,4-dibromobutane.—To a hot solution of 1.5 g. (0.025 mole) of potassium hydroxide in 40 ml. of absolute ethanol was added 2 g. (0.005 mole) of 1,4-dibenzoyl-1,4-dibromobutane, prepared from 1,4-dibenzoylbutane[13] by the method of Fuson and co-workers.[14] The mixture was refluxed for one hour, after which time it was evaporated to a volume of 25 ml. and cooled overnight. Filtration yielded a material which was triturated with warm water and recrystallized from ethanol; yield, 0.7 g., m. p., 137–140°. Similar results were obtained using methanol as a solvent. Three recrystallizations from ethanol raised the melting point to 139–140°. The substance was shown to be the compound (VII) originally obtained by Fuson and co-workers[8,9] upon treatment of dibenzoyldibromobutane with sodium cyanide and other alkaline type reagents. It was identified by a mixture melting point with a sample prepared by the method of Kao.[10]

Anal. Calcd. for $C_{18}H_{13}BrO_2$: C, 62.99; H, 4.41; Br, 23.3. Found: C, 62.62; H, 4.79; Br, 23.5.

When the reaction was repeated using a ratio of 12 parts of potassium hydroxide to 1 part of dibenzoyldibromobutane, only a dark colored resin was obtained.

Treatment of 1,4-dibenzoyl-1,4-dibromobutane with refluxing triethylamine with stirring for three hours gave a 50% recovery of starting material and a tar. When the reaction was carried out for twenty hours, only a tar was obtained.

Reduction of VII with zinc and acetic acid (heated over a steam-bath for fifteen minutes) yielded dibenzoylbutane (V). The reaction mixture was worked up as described in the zinc–acetic acid reduction of dibenzoylbutadiene. The dibenzoylbutane melted at 109–111° and was identified by a mixture melting point with an authentic sample.[13]

Summary

1,4-Dibenzoyl-1,3-butadiene has been made from muconic acid and its structure has been proved by reduction to 1,4-dibenzoylbutane and to 1,4-dibenzoyl-2-butene. Sunlight converts dibenzoylbutadiene to a dimer. Diazomethane reacts with it to give a bis-pyrazoline.

AUSTIN, TEXAS RECEIVED[15] FEBRUARY 28, 1949

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[13] Prepared by the method of Fuson and Walker in **Blatt**, "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 169.

[14] Fuson, Kuykendall and Wilhelm, THIS JOURNAL, **53**, 4190 (1931).

[15] Original manuscript received October 23, 1948.