prisms (0.8 g.), m.p. 196–198°, of **bis-(7,17-borazaro-5,6-dihydro-7-benz[a]anthryl) oxide (X)**. The carbon analyses were consistently low, probably due to partial hydration.

*Anal.* Calcd. for $C_{32}H_{26}N_2B_2O$: C, 80.7; H, 5.5; N, 5.9; mol. wt., 476. Found: C, 79.9; H, 5.8; N, 5.8; mol. wt. (Rast), 400.

**7-Phenyl-7,17-borazaro-5,6-dihydrobenz[a]anthracene.**—A solution of IX (4.6 g.) and phenyl dichloroboronite (7.4 g.) in decalin (50 ml.) was boiled under reflux with stirring for 3 hours after the initially formed complex had dissolved and then evaporated under pressure. The residue was treated with ice–cold potassium hydroxide solution (30%) and ether and the ether layer washed with hydrochloric acid, dilute alkali, and water, then dried and evaporated. The oily residue (1.8 g.) was chromatographed from benzene on alumina. The main fraction (480 mg.) crystallized from dry petroleum ether–benzene in almost colorless prisms, m.p. 178–180°, of **7-phenyl-7,17-borazaro-5,6-dihydrobenz-[a]anthracene (XI)**.

*Anal.* Calcd. for $C_{22}H_{18}NB$: C, 86.0; H, 5.9; N, 4.6. Found: C, 85.6; H, 6.1; N, 4.7.

On exposure to moist air the compound changed to a white insoluble powder, m.p. 305–307°. The same product was obtained by elution of the chromatographic column with methylene chloride.

**10-Benzylphenanthridine.**—A mixture of 2-phenylacetylamino-biphenyl (10 g.) phosphorus pentoxide (10 g.) and xylene (100 ml.) was boiled overnight and the solid residue then decomposed with strong potash solution. Isolation with ether gave **10-phenylphenanthridine (XIII)** (4.5 g.) which crystallized from methanol in needles, m.p. 109°–110°.

*Anal.* Calcd. for $C_{20}H_{15}N$: C, 89.2; H, 5.6; N, 5.2. Found: C, 89.1; H, 5.5; N, 5.4.

**1-(4-Bromo-1-butyl)-2-methyl-2,1-borazaronaphthalene and 1,4-Bis-(2-methyl-2,1-borazaro-1-naphthyl)-butane.**—A solution of methyllithium prepared from lithium (5.5 g.) and methyl iodide (40 g.) in dry ether was added dropwise to one of 2-methyl-2,1-borazaronaphthalene[9] (18 g.) in dry benzene with vigorous stirring at 20° until a permanent yellow color appeared. The resulting solution was added gradually to a solution of freshly distilled 1,4-dibromobutane (110 g.) in boiling benzene (200 ml.) and the mixture boiled 12 hours under reflux. After cooling and hydrolysis (dilute hydrochloric acid), the benzene layer was evaporated and the residue fractionated under reduced pressure. Fraction 1, b.p. 150–180°/(0.9 mm.) consisted of unchanged starting material (5 g.). Fraction 2 (10.5 g.), b.p. 190–195°/(0.7 mm.) consisted of 1-(4-bromo-1-butyl)-2-methyl-2,1-borazaronaphthalene (XVa) apparently contaminated by unsaturated products containing less bromine. The residue from the distillation crystallized from acetone in white needles (0.2 g.), m.p. 157–158° of **1,4-bis-(2-methyl-2,1-borazaro-1-naphthyl)-butane (XVI)**.

*Anal.* Calcd. for $C_{20}H_{26}N_2B_2$: C, 77.6; H, 7.4; N, 8.2. Found: C, 77.7; H, 7.6; N, 8.2.

**1-(4-N-Morpholino-1-butyl)-2-methyl-2,1-borazaronaphthalene.**—A solution of crude IV (2 g.) and morpholine (3 g.) in ethanol (100 ml.) was boiled under reflux for 24 hours then evaporated under reduced pressure and the residue treated with ether and 40% sodium hydroxide solution. Evaporation of the ether gave **1-(4-N-morpholino-1-butyl)-2-methyl-2,1-borazaronaphthalene (XVb)** as a pale yellow oil (1.2 g.), b.p. 190–195°(0.7 mm.), $n^{26}D$ 1.5689.

*Anal.* Calcd. for $C_{16}H_{25}N_2BO$: C, 71.9; H, 8.8; N, 9.8; B, 3.8. Found: C, 71.9; H, 9.0; N, 9.7; B, 4.0.

**1,2,3,4-Tetrahydro-12,11-borazarophenanthrene.**—Magnesium (3 g.) was added to a solution of crude IV (3 g.) in dry ether (200 ml.) with cooling (ice-bath). After 2 hours at room temperature the solution was boiled overnight under reflux, cooled, hydrolyzed with cold dilute hydrochloric acid and the ether layer dried (sodium sulfate) and evaporated. Fractionation of the residue in a bulb tube gave a colorless oil (1.6 g.), b.p. 150–155° (0.5 mm.) which crystallized on standing in a refrigerator, forming white needles, m.p. 26–28°, of **1,2,3,4-tetrahydro-12,11-borazarophenanthrene (XVII)**.

*Anal.* Calcd. for $C_{14}H_{14}NB$: C, 78.8; N, 7.8; N, 7.7; B, 5.9; mol. wt., 207. Found: C, 78.3; H, 8.0; N, 7.5; B, 5.6; mol. wt. (mass spec.), 207.

**12,11-Borazarophenanthrene.**—A mixture of VII (90.3 mg.), palladized charcoal (0.25 g., 10% Pd) and 1-hexene (1 ml.) was heated overnight in a sealed tube at 290–300° and the cold residue extracted with ether. Evaporation of the ether and chromatography from petroleum ether (b.p. 60–65°) benzene gave **12,11-borazarophenanthrene (XVIII)** (67 mg.) which crystallized from petroleum ether (b.p. 30–35°) in long white needles, m.p. 75–77°.

*Anal.* Calcd. for $C_{12}H_{10}NB$: C, 80.54; H, 5.59. Found: C, 80.57; H, 5.53.

**Acknowledgment.**—We are most grateful to Dr. S. Meyerson, of the American Oil Co., Whiting, Ind., for the mass spectrometric analysis of XVII.

---

[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

# Rearrangements of Benzeneazotribenzoylmethane and its Derivatives. Structural Reassignments[1]

BY DAVID Y. CURTIN AND MARVIN L. POUTSMA[2]

RECEIVED JULY 20, 1962

The coupling of benzenediazonium ion with tribenzoylmethane anion gives a product I which had previously been thought to be an O-azo compound A. It has now been found to be benzeneazotribenzoylmethane (B). The red rearrangement product II, obtained by heating the azo compound I, had been assigned the structure B. It has now been found to be the enol benzoate, α-benzeneazo-β-benzoyloxybenzalacetophenone. The enol benzoate II is converted with zinc and acetic acid to 2-benzoyl-3-phenylindole (XII). Catalytic reduction of the enol ester II gives benzamidodibenzoylmethane (XIV). Bromination of tribenzoylmethane in chloroform, carried out in order to prepare bromotribenzoylmethane as previously reported, gave instead bromodibenzoylmethane. Mesityleneazotribenzoylmethane, instead of undergoing the thermal rearrangements observed with the unsubstituted compound I, gives 5,7-dimethylindazole (XVIII) when heated either alone or in dioxane solution.

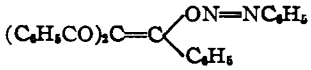
Dimroth and Hartmann,[3] in 1907, reported that the anion of tribenzoylmethane reacts with benzenediazonium ion in buffered aqueous solution to give a yellow product (I) assigned the structure A, which would result from a coupling reaction at an oxygen atom. Evidence for structure A was provided primarily by the observation that the substance I reverted readily to benzenediazonium ion. Thus, with cold ethereal hydrogen chlo-

---

[1] Supported in part by a grant (G-14,480) from the National Science Foundation. Taken from the Ph.D. Thesis of Marvin L. Poutsma, submitted to the University of Illinois, 1962, and presented at the 141st Meeting of the American Chemical Society, Washington, D. C., 1962.

[2] Roger Adams Fellow, 1958–1959. National Science Foundation Fellow, 1959–1961.

[3] O. Dimroth and M. Hartmann, *Ber.*, **40**, 2404, 4460 (1907); **41**, 4012 (1908).

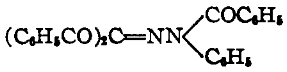


$(C_6H_5CO)_2C{=}C(ON{=}NC_6H_5)(C_6H_5)$

A

$(C_6H_5CO)_3CN{=}NC_6H_5$

B



$(C_6H_5CO)_2C{=}NN(COC_6H_5)(C_6H_5)$

III

ride compound I was converted to benzenediazonium chloride and tribenzoylmethane; with 2-naphthol in ethanol it gave 1-benzeneazo-2-naphthol and tribenzoylmethane; and in hot ethanol the products were tribenzoylmethane, nitrogen and acetaldehyde. When the yellow substance I was heated above 100° either alone or in solution it rearranged to a red isomer II to which the structure B was assigned. The red compound was difficult to isolate because it rearranged further on heating to give a white isomer III, shown to be diphenyltriketone *sym*-benzoylphenylhydrazone. In a later study,[4] the effect of substituents on the over-all rearrangement from I to III was examined.

The original structural assignments have been widely accepted,[5] but the unusual nature of the rearrangement of the azo compound II to the hydrazone III has prompted a further investigation of these reactions and the results obtained require a reassignment of the structures of I and II. Work preliminary to the kinetic investigation reported in the following paper showed that the previous assumption that the sequence of steps could not be

$$\text{I} \longrightarrow \text{II} \longrightarrow \text{III}$$

completely correct because the rearrangement of II to III was slower than the rearrangement of I to III. There must then be a direct pathway for the rearrangement of I to III without the intervention of II. While not impossible perhaps with the structures as previously assumed, such a rearrangement would appear to be improbable.

A further reason for questioning the structures of I and II came from an examination of the infrared spectra, which had not been available to the previous investigators. A solution of the yellow azo compound I in methylene chloride showed a strong absorption at 1675 cm.$^{-1}$ with a shoulder at 1700 cm.$^{-1}$. The spectra of tribenzoylmethane (IV) in dimethyl sulfoxide and also as a Nujol mull and potassium bromide disk were examined for comparison. The spectrum in dimethyl sulfoxide and also in Nujol showed absorption at 1675 with a shoulder at 1700 cm.$^{-1}$ very similar in appearance to the spectrum of I. The presence of the carbonyl absorption in the characteristic region and the absence of the very strong enol absorption at 1600 cm.$^{-1}$ or lower[6] suggests that the spectra of tribenzoylmethane (IV) so obtained are spectra of the triketo compound rather than the enol. Furthermore the Nujol mull showed no absorption in the region from 3100 to 3600 cm.$^{-1}$ characteristic of a hydroxyl group. The n.m.r. spectrum of a solution in dimethyl sulfoxide showed two multiplets centered at 2.33 and 1.88 $\tau$[7] with relative areas of 10.0:6.0. There was no absorption at lower field which might have been attributed to the hydrogen-bonded enol structure.[7] The ratio of the areas suggested that the tertiary hydrogen atom absorbed in the same region as nine of the aromatic protons, presumably the *meta* and *para* protons, at 2.33 $\tau$. Acidification of a solution of the potassium salt of tribenzoylmethane in deuterium oxide gave the expected decrease in the ratio to 9.2:6.0. Rapid precipitation of the tribenzoylmethane from an aqueous solution of its potassium salt gave a solid which when incorporated into a potassium bromide disk gave both the bands at 1675 and 1700 and very broad and intense absorption centered at 1540 cm.$^{-1}$ suggesting that in this case some of the enol was present. The agreement of the spectrum of the yellow azo compound I with that of tribenzoylmethane indicated that its structure had been incorrectly assigned and that it was, in fact, benzeneazotribenzoylmethane (B), presumably the more stable *trans* isomer. Ultraviolet and visible absorption maxima were found at 255 m$\mu$ ($\epsilon$ 3.12 × 10$^4$) (inflection near 280–290 m$\mu$) and at 424 m$\mu$ ($\epsilon$ 296). The absorption at 424 m$\mu$ can be compared with benzeneazomethane (V) ($\lambda_{max}$ 404 m$\mu$, $\epsilon$ 87 in cyclohexane),[8] benzeneazo-*t*-butane (VI) ($\lambda_{max}$ 407, $\epsilon$ 144 in ethanol)[9] and benzeneazotriphenylmethane (VII) ($\lambda_{max}$ 421, $\epsilon$ 180 in hexane),[8] each of which has the azo-linkage conjugated with a phenyl group at one end and unconjugated at the other. The band at 255 m$\mu$ is also reasonable since benzeneazomethane has a corresponding band at 260 m$\mu$ ($\epsilon$ 7800)[8] and the diketo form of benzoylacetone (in ethanol) shows its corresponding absorption at 247 ($\epsilon$ 13,000).[10]

$(C_6H_5CO)_3CH$

IV

$C_6H_5N{=}NCH_3$

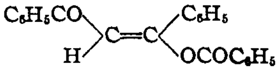
V

$C_6H_5N{=}NC(CH_3)_3$

VI

$C_6H_5N{=}NC(C_6H_5)_3$

VII



$(C_6H_5CO)(H)C{=}C(C_6H_5)(OCOC_6H_5)$

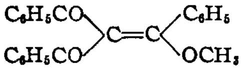
VIII

$C_6H_5N{=}NCH{=}CHCH_3$

IX

$C_6H_5N{=}NCH{=}CHN{=}NC_6H_5$

X



$(C_6H_5CO)_2C{=}C(C_6H_5)(OCH_3)$

XI

The assignment of structure B to the yellow substance I leaves the structure of the red isomer II to be redetermined. The infrared spectrum of this compound showed strong absorption at 1745 cm.$^{-1}$ and another slightly less intense absorption at 1675 cm.$^{-1}$. This is clearly inconsistent with the previously assigned tribenzoylmethane structure B in the light of the complete lack of similarity of the absorption to that in the carbonyl region of

---

[4] D. Y. Curtin and C. S. Russell, *J. Am. Chem. Soc.*, **73**, 5160 (1951).

[5] See for example, R. R. Phillips, "Organic Reactions," Vol. X, R. Adams, Editor-in-Chief, John Wiley and Sons, Inc., New York, N. Y., 1959, p. 145 ff.

[6] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 142, 143.

[7] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 71.

[8] A. Burawoy, *J. Chem. Soc.*, 1867 (1937); see H. Zollinger, "Diazo and Azo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, chapt. 13.

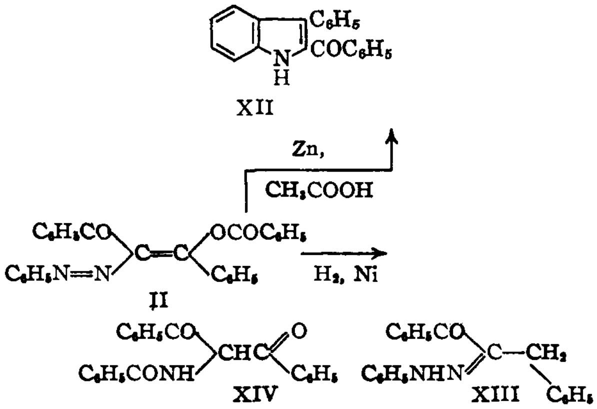
[9] R. O'Connor, *J. Org. Chem.*, **26**, 4375 (1961).

[10] A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold, Ltd., London, 1954, pp. 228, 229.

tribenzoylmethane discussed above. The absorption at 1745 cm.$^{-1}$ is suggestive of the presence of an enol benzoate; and the infrared spectrum of the benzoate ester VIII of dibenzoylmethane enol, prepared as a model compound, showed absorption at 1749 and 1670 cm.$^{-1}$.

The ultraviolet and visible spectra of the red compound II are in better agreement with the enol benzoate structure than with the triketo structure B previously assigned. It showed $\lambda_{max}$ 452 m$\mu$, $\epsilon$ 597, more consistent with a molecule conjugated at each end of the azo linkage (compare azobenzene with $\lambda_{max}$ 445 m$\mu$, $\epsilon$ 300) than with a structure conjugated at one end such as B (compare V–VII, discussed above).[8,10,11] Two other absorption maxima at 243 m$\mu$ ($\epsilon$ 34,500) and at 348 m$\mu$ ($\epsilon$ 23,900) are also quite consistent with the $\alpha,\beta$-unsaturated ketone structure II. In support of this conclusion may be cited the spectra of the azo-olefins IX and X with maxima at 316 m$\mu$ and 370 m$\mu$ ($\epsilon$ 16,000 and 39,000, respectively)[12] and the spectrum of the enol ether XI which was prepared from tribenzoylmethane with silver iodide and had $\lambda_{max}$ 252 m$\mu$ ($\epsilon$ 22,300) with a broad shoulder at 290 m$\mu$ and beyond.

Two reactions of the red O-benzoyl compound II are of interest in their own right but do little to distinguish between the two structures being considered. Reduction with zinc and acetic acid led to a product shown by its infrared spectrum and later a direct comparison with an authentic sample to be 2-benzoyl-3-phenylindole (XII). A number of possible routes from II to XII involving at some point a Fischer indole synthesis[13] can be formulated. The only information about the mechanism provided by the present work is that benzyl phenyl diketone phenylhydrazone (XIII) is not an intermediate since it fails to yield the indole XII under the conditions employed in the reaction of II. It can, be converted to II by more vigorous treatment, however.


XII

II

XIV

XIII

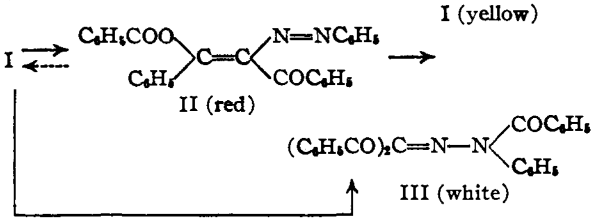
Catalytic reduction of the enol ester II with Raney nickel gave benzamidodibenzoylmethane (XIV), identical with an authentic sample prepared from oximinodibenzoylmethane by reduction and benzoylation. The formation of the diketo amide XIV could, of course, be formulated as a reductive cleavage of the azo linkage followed by a benzoyl migration from either structure previously considered for the red azo compound II.

In view of the modifications required for the structures of the two azo compounds I and II, the structure previously assigned[3] to the hydrazone III was also investigated. The original assignment was reaffirmed by the synthesis of III from diphenyl triketone *sym*-phenylhydrazone and benzoyl chloride in pyridine.

The revised sequence of reactions is summarized below. In the paper which follows are reported results of a more detailed study of these rearrangements.

$$(C_6H_5CO)_3C^- + C_6H_5N{\equiv}N^+ \longrightarrow (C_6H_5CO)_3CN{=}NC_6H_5$$

I (yellow)


II (red)

III (white)

During the search for model compounds, the synthesis of bromotribenzoylmethane (XV), which had been reported by Werner[14] to be obtained by bromination of tribenzoylmethane in chloroform, was repeated. The product found, instead of that previously reported, was bromodibenzoylmethane (XVI), identical with the product obtained by bromination of dibenzoylmethane in acetic acid.

$(C_6H_5CO)_3CBr$ XV $\quad$ $(C_6H_5CO)_2CHBr$ XVI

The only structural evidence previously advanced[14] was a bromine analysis of 22.6% whereas the calculated value for the tribenzoyl compound XII is 19.7% and that for the dibenzoyl compound is 26.4%. It seems likely therefore that the product reported by Werner was at best a mixture of XV and XVI and that his bromination reaction like ours was accompanied by a debenzoylation reaction catalyzed by hydrogen bromide liberated during the bromination.

An attempt to carry out the rearrangement of mesityleneazotribenzoylmethane (XVII) deserves special mention. Instead of products analogous to those found in the rearrangement of the parent compound I, when XVII was heated as a solid or in dioxane solution at 100° the only products isolated were tribenzoylmethane and 5,7-dimethylindazole (XVIII) in yields as high as 67 and 65%. The indazole XVIII had been prepared in 5% yield by Bamberger[15] by treatment of mesitylenediazonium chloride with strong base. Repetition of the reaction, modified by use of a two-phase system to remove the product immediately from the diazonium salt which is known to couple with it, gave the indazole XVIII in only 9% yield. The formation of the indazole XVIII is reminiscent of the conversion of *o*-methylbenzenediazoacetates to indazoles.[16]

---

[11] Reference 10, p. 236.

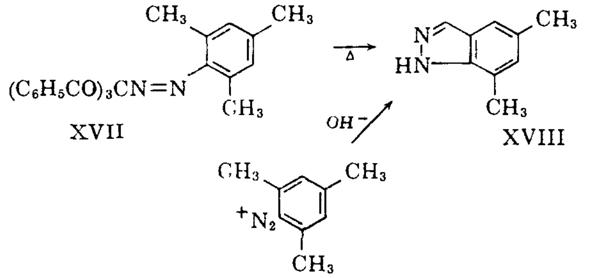
[12] P. Grammaticakis, *Bull. soc. chim. France*, [5] 15, 985 (1948).

[13] See T. S. Stevens, "Chemistry of Carbon Compounds," Vol. IVA, Edited by E. H. Rodd, Elsevier Publishing Co., New York, N. Y., 1957, pp. 72, 73.

[14] A. Werner, *Ber.*, 39, 1289 (1906).

[15] E. Bamberger, *Ann.*, 305, 308 (1899).

[16] P. Jacobsen and L. Huber, *Ber.*, 41, 660 (1908); R. Huisgen and H. Nakaten, *Ann.*, 586, 84 (1954).



It may be noted that the revision of the structure of I from an O-azo to a C-azo compound suggests that a number of other compounds assigned[3,4] the O-azo structure should be reinvestigated and the structures in many if not all cases similarly revised. Among these are at least twelve coupling products of benzenediazonium ion or its *p*-bromo or *p*-nitro derivative with variously substituted tribenzoylmethanes,[3,4] acetyldibenzoylmethanes,[3] benzoyldiacetylmethane,[17] dibenzoylacetic esters[3,18] and benzoylmalonic ester.[3] It is of interest that those reports published before October, 1908, had assigned to the coupling products which had been prepared at the time the probably correct C-azo structures but these were modified to the O-azo structures[3] by analogy with the parent tribenzoylmethane product 1.

## Experimental[19]

**Tribenzoylmethane**, m.p. 227–230° (lit.[21] m.p. 228–231° in glass tubes) was prepared in 47% yield from dibenzoylmethane and benzoyl chloride with sodium ethoxide.[21] Recrystallization from benzene gave triketone, m.p. 242–243.5°. The infrared spectrum either in dimethyl sulfoxide solution or as a Nujol mull showed strong absorption at 1675 cm.$^{-1}$ with a shoulder at 1700 cm.$^{-1}$ and a sharp band of medium intensity at 1602 cm.$^{-1}$. The ultraviolet spectrum in dioxane showed $\lambda_{max}$ 252 m$\mu$, $\epsilon$ 27,500, and $\lambda_{max}$ 324 m$\mu$, $\epsilon$ 8320. The n.m.r. spectrum in dimethyl sulfoxide solution contained two well-separated multiplets at 1.87 $\tau$ and 2.28 $\tau$ with relative areas of 6.0:10.0 (calculated assuming a total of 16 protons absorbing). Conversion to the enol was carried out by treatment of a mixture of the triketone with an equal weight of potassium carbonate in boiling ethyl acetate for 1 hr. Extraction with water and precipitation with acid gave a solid, probably the enol contaminated with some triketone as shown by the presence in the infrared spectrum (potassium bromide disk) of the characteristic triketone bands plus additional strong absorption at 1650, very strong absorption at 1600 and a very broad band at 1550 cm.$^{-1}$. The enol prepared as above but in deuterium oxide (>99.5%) D and by acidification with an acid mixture prepared from acetyl chloride and deuterium oxide was dried and then heated for 1 hr. at 100° in dimethylsulfoxide solution to allow ketonization. It showed two well-separated multiplets at 1.88 and 2.33 $\tau$ with relative areas of 6.4:8.6 (assuming 15 protons were responsible for the absorption).

**Benzeneazotribenzoylmethane** (I).—The coupling of benzenediazonium fluoborate (3.0 g., 0.016 mole) with the potassium salt of tribenzoylmethane prepared from 10.0 g. (0.030 mole) of triketone, 10.0 g. of potassium carbonate and 1.0 l. of ethyl acetate for 1 hr. under reflux and then extraction into cold water, was carried out at 0° in a solution at *p*H 8–9 to give a yellow oil which after 5 min. was extracted with ether. Concentration (at a temperature below 30°) of the dried ether extracts to 150 ml. gave 4.45 g. of azotriketone I and dilution of the filtrate with hexane gave an additional 1.29 g. Yields with this procedure were 45–84%. The product was purified by recrystallization from ether (between 25° and 0°). The m.p. varied with the rate of heating. On a microscope hot-stage it became noticeably orange at 115°, liquefied at 121–123° to an orange-red melt, resolidified at 128°–180°, at which temperature the color had faded. The solid remelted at 197–200°. The infrared spectrum in methylene chloride showed a strong absorption maximum at 1675 with a shoulder at 1700 cm.$^{-1}$ and a sharp band of medium intensity at 1597 cm.$^{-1}$. The ultraviolet-visible spectrum in dioxane showed $\lambda_{max}$ 255 m$\mu$, $\epsilon$ 31,200, with an inflection at 280 m$\mu$ and $\lambda_{max}$ 424 m$\mu$, $\epsilon$ 296.

The azotriketone I was readily cleaved by basic media to diphenyltriketone *sym*-phenylhydrazone. Thus 100 mg. of I with 40 mg. of sodium in 1.0 ml. of absolute ethanol gave after 5 min., on neutralization with acetic acid, 35 mg. of orange phenylhydrazone, m.p. 151.5–153° (lit.[22] m.p. 153–154°). Attempts to purify the azo triketone I by chromatography over Florisil, Woelm neutral alumina or alumina neutralized with ethyl acetate and activated at 130° for 3 hr. all produced small amounts of the hydrazone. Finally, treatment of 443 mg. (1.03 mmoles) of I with 38.0 mg. (1.13 mmoles) of 95% hydrazine and 35 ml. of ethanol for 30 min. produced 265 mg. (79%) of hydrazone, m.p. 151.5–153°. In each of these cases the product was shown by a mixed m.p. and comparison of the infrared spectra to be identical with an authentic sample.[22]

Reaction of 216 mg. of azotriketone I in 10 ml. of chloroform with 0.030 ml. of bromine gave 71 mg. of benzenediazonium perbromide, m.p. 62° dec., infrared absorption at 2270 cm.$^{-1}$, and 91 mg. (56%) of tribenzoylmethane, m.p. 228–234°.

**$\alpha$-Benzeneazo-$\beta$-benzoyloxybenzalacetophenone** (II).—A solution of 505 mg. (1.17 mmoles) of benzeneazotribenzoylmethane in 1.25 ml. of dioxane was heated under reflux for 30 min. The bright red solution was poured onto a column of 50 g. of Florisil packed in hexane. Elution with hexane and then with methylene chloride–hexane 1:1 gave a red oil which crystallized. After washing with a small amount of ether there was obtained 102 mg. of red crystalline solid, m.p. 160.5–162° (placed in the bath at 157° and heated at a rate of 2°/min.). Dilution of the filtrate with hexane gave 26 mg. of the product II, m.p. 161–162° (lit.[3] 164°). The product when recrystallized from acetone (operating between 25° and 0°) had m.p. 162.5–163°. The yield of 25% was duplicated closely in several reactions. The infrared spectrum in methylene chloride had maxima at 1745, 1675, 1615 and 1597 cm.$^{-1}$. The ultraviolet-visible spectrum in dioxane had $\lambda_{max}$ 242 m$\mu$, $\epsilon$ 34,500; $\lambda_{max}$ 348 m$\mu$, $\epsilon$ 23,900; and $\lambda_{max}$ 452 m$\mu$, $\epsilon$ 597.

**Diphenyltriketone *sym*-benzoylphenylhydrazone** (III) was prepared by heating 1.00 g. (2.26 mmoles) of benzeneazotriketone I at 120° for 18 hr. to give 0.62 g. of product, m.p. 198–200° (lit.[3] 203°). Crystallization from methanol gave m.p. 199–200.5°. The infrared spectrum in chloroform showed maxima at 1674 and 1595 cm.$^{-1}$. The ultraviolet spectrum in dioxane had $\lambda_{max}$ 233 m$\mu$, $\epsilon$ 25,900; $\lambda_{max}$ 260 m$\mu$, $\epsilon$ 26,000. The same product III, m.p. 199–200°, was obtained in 46% yield by benzoylation with 290 mg. (2.1 mmoles) of benzoyl chloride in 10 ml. of pyridine for 1 week at room temperature; 656 mg. (2.0 mmoles) of diphenyltriketone *sym*-phenylhydrazone.[22]

**$\beta$-Benzoyloxybenzalacetophenone** (VIII), m.p. 97–99°, was prepared in 80% yield by the benzoylation[23] of dibenzoylmethane. Further recrystallization from ethanol raised the m.p. to 100–101.5° (lit.[23] 108–109°). The infrared spectrum in carbon disulfide showed maxima at 1749, 1670, 1607 and 690 cm.$^{-1}$. The n.m.r. spectrum in carbon disulfide showed multiplets centered at 2.02, 2.27 and 2.61 $\tau$ and a sharp singlet with a relative area of 1.1/16 at 2.84 $\tau$.

---

[17] K. Auwers and A. Bennecke, *Ann.*, **378**, 243 (1910).

[18] C. Bülow and E. Hailer, *Ber.*, **32**, 2880 (1899).

[19] All melting points are corrected. Microanalyses were determined by Mr. J. Nemeth, Mr. G. Callahan, Mrs. M. Weatherford, Mrs. A. Bay and Miss J. Liu. Infrared spectra were measured with a Perkin-Elmer model 21 spectrophotometer with sodium chloride optics by Mr. P. McMahon, Mr. D. Johnson, Miss D. Wood and Mr. W. Dalton. The n.m.r. spectra were obtained by Mr. O. W. Norton with a Varian HR 60 spectrophotometer. Spectra are reported in $\tau$ units.[20] Ultraviolet and visible spectra were measured with a Cary model 14M spectrophotometer. Ultraviolet, infrared and n.m.r. spectra are available in the Ph.D. thesis already referred to, available from Univ. Microfilms, Ann Arbor, Mich.

[20] G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

[21] L. Claisen, *Ann.*, **291**, 25 (1896); see also W. Dieckmann, *Ber.*, **49**, 2210 (1916).

[22] C. Beyer and L. Claisen, *Ber.*, **21**, 1703 (1888).

[23] L. Claisen and E. Haase, *ibid.*, **36**, 3679 (1903).

**α-Benzoyl-β-methoxybenzalacetophenone (XI).**—A mixture of 2.00 g. (6.10 mmoles) of tribenzoylmethane, 2.0 g. of potassium carbonate, 4.0 g. of silver oxide and 30 ml. of methyl iodide was heated under reflux for 6 hr. The insoluble residue was filtered, the filtrate washed with dilute sodium carbonate and water, dried and evaporated to give a clear oil which crystallized when treated with 10 ml. of ether to give 1.05 g. (50%) of white product XI, m.p. 97–99.5°. Crystallization from ether gave a m.p. of 100–101°. The infrared spectrum in methylene chloride had peaks at 1668, 1635 and 1603 cm.$^{-1}$. The ultraviolet spectrum in cyclohexane solution showed $\lambda_{max}$ 252 mμ (ε 22,300). The n.m.r. spectrum in methylene chloride showed a singlet at 6.73 τ. The enol ether XI was cleaved to tribenzoylmethane by treatment for 5 min. with hot 0.5% methanolic hydrochloric acid.

*Anal.* Calcd. for $C_{23}H_{18}O$: C, 80.7; H, 5.3. Found: C, 80.9; H, 5.3.

**Cyclization of Benzyl Phenyl Diketone Phenylhydrazone. 2-Benzoyl-3-phenylindole (XII).**—When 144 mg. (0.46 mmole) of benzyl phenyl diketone phenylhydrazone in 15 ml. of acetic acid was heated under reflux for 24 hr. and the solvent removed under reduced pressure there was obtained after crystallization of the residue from cyclohexane 45 mg. (33%) of the indole XII as light tan crystals, m.p. 203.5–205°. A m.p. of a mixture with the substance obtained from reduction of II with zinc and acetic acid was undepressed and their infrared spectra were identical. An attempt to carry out this reaction with zinc chloride gave the product in only 2% yield.

**Reduction of the Enol Benzoate II with Zinc and Acetic Acid. 2-Benzoyl-3-phenylindole (XII).**—A solution of 389 mg. (0.90 mmole) of enol benzoate II in 80 ml. of glacial acetic acid was stirred with a large excess of reagent-grade zinc dust at 25° for 30 minutes. After filtration of the undissolved solid and dilution of the filtrate with water there was obtained 84 mg. of solid, m.p. 202–204°. Crystallization from ethanol gave 63 mg. (24%) of the indole XII, m.p. 205.5–206.0°, as pale yellow crystals. The infrared spectrum (potassium bromide disk) showed absorption at 3290 and 1615 cm.$^{-1}$. The ultraviolet spectrum in ethanol had $\lambda_{max}$ 250 mμ, ε 21,000, and $\lambda_{max}$ 328 mμ, ε 15,000. The same product, m.p. 203.5–205°, was obtained in 33% yield from 144 mg. of benzyl phenyl diketone phenylhydrazone (described below) by heating a solution in 15 ml. of acetic acid under reflux for 24 hr. and removal of the solvent by distillation under reduced pressure. The identity was shown by non-depression of the m.p. of a mixture of the two samples and by their essentially identical infrared spectra.

*Anal.* Calcd. for $C_{21}H_{15}NO$: C, 84.8; H, 5.1; N, 4.7. Found: C, 84.4; H, 5.2; N, 4.8.

**Benzyl Phenyl Diketone Phenylhydrazone.**—From 1.34 g. of benzyl phenyl diketone in 10 ml. of 95% ethanol with 650 mg. of freshly distilled phenylhydrazine and 0.2 ml. of acetic acid was obtained by heating at 70–80° for 30 min., addition of water and cooling to 0°, 1.39 g. of yellow crystals, m.p. 101–104°. Crystallization from ethanol gave 1.22 g. (65%) of hydrazone, m.p. 105.5–107°. The infrared spectrum in chloroform showed maxima at 1668 and 1635 cm.$^{-1}$ but none near 1700 cm.$^{-1}$, suggesting that the carbonyl adjacent to the benzyl group is the one which reacted.

*Anal.* Calcd. for $C_{21}H_{18}N_2O$: C, 80.2; H, 5.8; N, 8.9. Found: C, 80.5; H, 5.8; N, 8.7.

**Catalytic Reduction of the Enol Benzoate II. Benzamidodibenzoylmethane (XIV).**—From a solution of 152 mg. (0.35 mmole) of enol benzoate II in 40 ml. of ethyl acetate there was obtained by hydrogenation at 6 p.s.i. over Raney nickel, filtration of the catalyst and evaporation of the filtrate, a yellow oil from which 22 mg. of crystals, m.p. 169–172°, was obtained after recrystallization from ether-hexane. Further recrystallization from cyclohexane raised the m.p. to 173.5–174.5°. The infrared spectrum (potassium bromide disk) showed maxima at 3280, 1700, 1668, 1635, 1600, 1583 and 1530 cm.$^{-1}$. The substance was identical as shown by a m.p. of a mixture and comparison of the infrared spectra with a sample of benzamidodibenzoylmethane, m.p. 172.5–174.5°, prepared by reduction of 3.33 g. of oximinodibenzoylmethane[24] and benzoylation as described below.

*Anal.* Calcd. for $C_{22}H_{17}NO_3$: C, 77.0; H, 5.0; N, 4.1. Found: C, 77.2; H, 5.1; N, 3.8.

**Reduction of Oximinodibenzoylmethane. α-Aminodibenzoylmethane and α-Benzamidodibenzoylmethane (XIV).**—A mixture of 3.33 g. (13.2 mmoles) of oximinodibenzoylmethane and 40 ml. of acetic acid was treated with 7.0 g. of stannous chloride dihydrate in 18 ml. of concentrated hydrochloric acid at 25–30° for 15 hr. after which 3 g. of tin metal was added and the stirring continued for 8 hr. Filtration gave, after washing with a small amount of 1:1 acetic–hydrochloric acid, 1.97 g. of solid amine salt, melting above 197°. Treatment of a small amount with one equivalent of sodium ethoxide gave the free amine as white needles, m.p. 122–123.5°.

*Anal.* Calcd. for $C_{15}H_{13}NO_2$: C, 75.3; H, 5.5; N, 5.9. Found: C, 75.5; H, 5.8; N, 5.7.

When 540 mg. of the crude amine salt in 20 ml. of tetrahydrofuran was treated with 0.30 ml. of benzoyl chloride and 0.57 ml. of triethylamine at room temperature for 15 hr. and the mixture diluted with water, there was obtained the white crystalline amide XIV (488 mg., m.p. 160–170°, with traces remaining solid to 260°) which after purification by crystallization from cyclohexane amounted to 250 mg. of amide, m.p. 172.5–174.5°.

**Reaction of the Enol Benzoate II with Bromine.**—A solution of 139 mg. (0.32 mmole) of II in 10 ml. of chloroform was treated with 51.5 mg. (0.32 mmole) of bromine for 1 hr. at 0° at 4.5 hr. at 25° at which time the red color had almost disappeared. The chloroform solution was washed with aqueous sodium bisulfite, dried and evaporated to leave an oil which crystallized to yield 100 mg. of a solid, m.p. 148–151.5°, collected by addition of a small amount of hexane and filtration. Crystallization from ether-hexane produced 78 mg. (60%) of a bright yellow monobromo derivative of diphenyltriketone *sym*-phenylhydrazone. An analytical sample crystallized from ethanol had m.p. 151.5–152.7°. The ultraviolet spectrum in ether had $\lambda_{max}$ 240 mμ, ε 16,900, and $\lambda_{max}$ 379 mμ, ε 15,700. The infrared absorption at 3200 cm.$^{-1}$ (very broad) and the carbonyl absorption at 1654 cm.$^{-1}$ resembled the corresponding absorptions at 3200 and 1645 cm.$^{-1}$ (sh. 1655 cm.$^{-1}$) in diphenyltriketone *sym*-phenylhydrazone and suggest that the product may be a ring-brominated triketone *sym*-phenylhydrazone. Its structure was not established however.

*Anal.* Calcd. for $C_{21}H_{15}N_2O_2Br$: C, 61.9; H, 3.7; N, 6.9. Found: C, 61.7; H, 3.7; N, 7.0.

**Bromination of Tribenzoylmethane.**—When 660 mg. (2.0 mmoles) of tribenzoylmethane in 14 ml. of chloroform was treated with 320 mg. (2.0 mmoles) of bromine with warming, the solid dissolved and the bromine color disappeared. After 15 min. the solution was washed with aqueous sodium bicarbonate and water, dried and evaporated to give a clear oil which crystallized when treated with hexane to give 3.88 mg. of white solid, m.p. 87.5–89°. Two recrystallizations from ethanol gave m.p. 89–90.3°. A m.p. of a mixture with dibenzoylbromomethane, m.p. 90–91.2°, prepared by the bromination[24] of dibenzoylmethane, showed no depression and the infrared spectra of the two samples were essentially identical.

*Anal.* Calcd. for $C_{15}H_{11}O_2Br$: C, 59.4; H, 3.7. Found: C, 59.5; H, 3.8.

**Mesityleneazotribenzoylmethane (XVII)** was prepared from the potassium salt of tribenzoylmethane [from 2.0 g. (6.0 mmoles) of tribenzoylmethane as described for the unsubstituted azo compound I] and the diazonium solution prepared from 540 mg. (4.0 mmoles) of mesidine[25] in 4 ml. of 20% hydrochloric acid and 276 mg. (4.0 mmoles) of sodium nitrite in 1 ml. of water at 0° which was then adjusted to *p*H 8–9. After 5 min. the mixture was filtered to give an orange gum which was dissolved in ether, the solution washed, dried and evaporated to give 872 mg. of a yellow-orange glass which produced 543 mg. (28%) of light orange crystals by crystallization from ether–hexane between 30 and 0°. The azo compound softened at 100–110°, resolidified, and remelted at 200–215°. It gave a bright red color with ethanolic 2-naphthol. The infrared spectrum (potassium bromide disk) showed maxima at 1670 (sh. at 1700) and 1597 cm.$^{-1}$.

---

[24] R. de Neufville and H. von Pechmann, *Ber.*, **23**, 3377 (1890).

[25] H. Conroy and R. A. Firestone, *J. Am. Chem. Soc.*, **78**, 2290 (1956).

*Anal.* Calcd. for $C_{21}H_{26}N_2O_3$: C, 78.5; H, 5.5; N, 5.9. Found: C, 78.4; H, 5.8; N, 5.5.

**Thermal Decomposition of Mesityleneazotribenzoylmethane (XVII).**—A solution of 204 mg. (0.43 mmole) of XVII in 15 ml. of dry dioxane, heated under reflux for 4 hr. and the dioxane evaporated, left after trituration of the residue with 60 ml. of benzene, 53 mg. of tribenzoylmethane, m.p. 232–234°. An additional 41 mg. (or a total of 67%) of triketone, m.p. 229–232°, was obtained from the benzene filtrate. Extraction of the filtrate with 10% hydrochloric acid followed by neutralization of the aqueous extracts, extraction with ether and evaporation of the ether left 41 mg. (65%) of 5,7-dimethylindazole, (XVIII), m.p. 133–134° (lit.[15] 133–134°). The same product, m.p. 134.5–135°, was obtained in 39% yield together with a 57% yield of tribenzoylmethane when azotribenzoylmethane XVII was heated at 100° without a solvent for 6 hr. For comparison the indazole XVIII m.p. 131.5–132.5°, was prepared (in 9% yield) by a modification of the method of Bamberger.[15] The identity of the samples was established by comparison of their infrared spectra (potassium bromide disks) and mixture melting points.

---

[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

# Rearrangements of Benzeneazotribenzoylmethane.[1] 1,3-Benzoyl Migrations from Carbon to Oxygen and from Carbon to Nitrogen

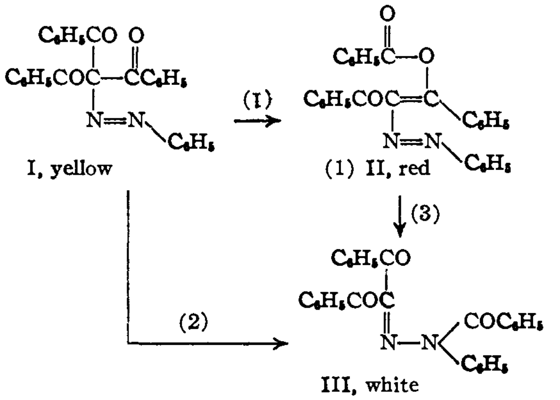
BY DAVID Y. CURTIN AND MARVIN L. POUTSMA[2]

RECEIVED JULY 20, 1962

Benzeneazotribenzoylmethane (I) has been found to undergo competing first-order rearrangements to α-benzeneazo-β-benzoyloxybenzalacetophenone (II) and diphenyltriketone *sym*-benzoylphenylhydrazone (III) with rates of 1.67 × $10^{-5}$ and 1.72 × $10^{-5}$ sec.$^{-1}$ in dioxane at 58.8°. At 97.1° II rearranges to III with a first-order rate constant of 1.48 × $10^{-5}$ sec.$^{-1}$. Extrapolation to 97.1° of the rates of formation of II and III from I gives for the processes I → II:I → III: II → III relative rates of 55:60:1. The process II → III is quite insensitive to solvent ionizing power as shown by an estimate of its rate in dioxane–water (80:20) compared to the rate in dioxane. The reaction rates of the *p*-methoxy, *p*-nitro and 2,4,6-trichloro-substituted benzeneazo analogs of I and II have been measured with the result that all three processes are accelerated by the nitro and trichloro substituents and retarded by the *p*-methoxyl group. The evidence available appears to be most readily explained in terms of an intermediate between I and II or III (and between II and III). The rearrangements of I and II occur in the solid state and preliminary results suggest that the ratio of products from I is different (II/III = 0.7) from that obtained from the melt or in dioxane solution (II/III = 1).

The yellow coupling product obtained from tribenzoylmethane with benzenediazonium ion was shown to rearrange when heated either in solution in a non-hydroxylic solvent or in the absence of a solvent first to a red substance and finally to a white product.[3,4] The structures of two of these substances which had been incorrectly assigned have been corrected in the preceding paper[5] and the sequence of reactions is that represented below. Rearrangement of benzeneazotribenzoylmethane (I) to either the enol benzoate II or to the hydrazone III represents a migration of a benzoyl group to an oxygen or nitrogen atom so placed that a 1,3-shift is involved. The scarcity of related 1,3-rearrangements has made a more detailed study desirable.

In order to unravel the relationships between the reactions interconverting the compounds I, II and III and to establish the kinetic orders of these processes, a study of their rates was undertaken. A convenient analytical procedure for the determination of the C-azo compound I was based on the observation[3] that it readily reverted in polar solvents to benzenediazonium ion and tribenzoylmethane. The benzenediazonium ion was then coupled with 2-naphthol-3,6-disulfonic acid disodium salt (R salt) and the coupling product determined from the absorbance at 510 mμ, where neither of the other products II and III absorb. Absorbance at 470 mμ was due to the two azo compounds I and II but not to the hydrazone III. The product II was determined by the absorbance at 470 mμ after a correction for the absorbance due to the starting material I determined as just indicated. The disappearance of the benzeneazo compound I in dioxane at 58.80° was first order when followed to greater than 90% completion. The relative amounts of enol benzoate II and hydrazone III remained constant throughout a run and the enol benzoate II was shown to be converted to the hydrazone III to a negligible extent in the time required for conversion of I to the mixture (nearly 1/1) of II and III. It can be concluded that the azo triketone I is undergoing two competing first-order reactions to give products II and III which are stable under the reaction conditions. On this basis the first-order rate constant for the disappearance of I has been partitioned to



---

(1) Supported in part by a grant (G-14,480) from the National Science Foundation. Taken from the Ph.D. Thesis of Marvin L. Poutsma, submitted to the University of Illinois, 1962. Presented at the 141st Meeting of the American Chemical Society, Washington D. C., 1962.

(2) Roger Adams Fellow, 1958–1959; National Science Foundation Fellow, 1959–1961.

(3) O. Dimroth and M. Hartmann, *Ber.*, **40**, 2404, 4460 (1907); **41**, 4012 (1908).

(4) D. Y. Curtin and C. S. Russell, *J. Am. Chem. Soc.*, **73**, 5160 (1951).

(5) D. Y. Curtin and M. L. Poutsma, *ibid.*, **84**, 4887 (1962).