

tallization from alcohol, had a m.p. and mixed m.p. of 93–94°.

Half of fraction (b) was extracted with four 20-ml. portions of 5% sodium bisulfite, and half of the bisulfite solution was treated with twice its volume of dinitrophenylhydrazine solution. There was obtained 1.24 g. of 2-hexanone 2,4-dinitrophenylhydrazone, orange-red rods of m.p. 104–105°, after recrystallization from alcohol. An attempted acylation of (b) after being washed with bisulfite using 2 g. of 3,5-dinitrobenzoyl chloride and 5 ml. of pyridine gave less than 15 mg. of yellow solid, m.p. 29–32°.

The clear, brown oily residue (c) was dissolved in 15 ml. of benzene and extracted with five 10-ml. portions of 5% bisulfite solution. From the aqueous extract was obtained, as before, 2.26 g. of 2-thienyl methyl ketone *p*-nitrophenylhydrazone, red needles from nitromethane, m.p. and mixed m.p. 181–182°. Reaction of the benzene solution with 3,5-

dinitrobenzoyl chloride gave less than 10 mg. of yellow solid, m.p. 70–78°. From 2.81 g. of unrecovered thienyl methyl ketone was obtained 0.108 g. (10.6%) of acetaldehyde, 77 mg. (7.2%) of ethanol and 1.77 g. (76.5%) of 2-hexanone.

When the desulfuration was repeated using nickel which had been washed free of water with isopropyl alcohol rather than ethanol, and then washed free of alcohol by xylene, there was obtained a 12.5% conversion to acetaldehyde, 9.2% to ethanol and 63.5% to 2-hexanone. There was no evidence for the presence of either isopropyl alcohol or acetone in the reaction mixture. Distillation of the xylene in which the nickel had been stored for two days between preparation and use showed no evidence for the presence of either alcohols or carbonyl compounds.

EVANSTON, ILLINOIS

RECEIVED MARCH 12, 1951

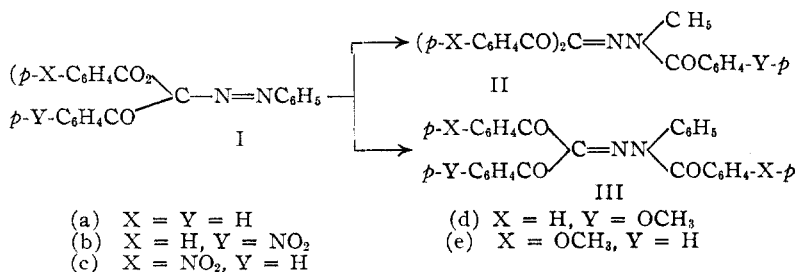
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

## The Effect of Substituents on the Thermal Rearrangement of Phenylazotribenzoylmethanes<sup>1a</sup>

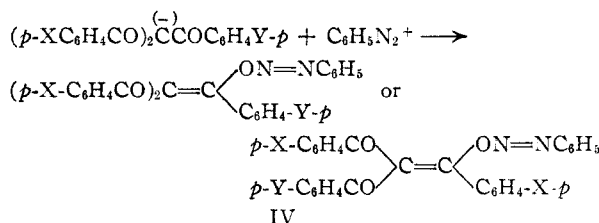
BY DAVID Y. CURTIN<sup>1b</sup> AND CHARLOTTE SANANES RUSSELL

The effect of *p*-nitro and *p*-methoxyl substituents on the thermal rearrangement of phenylazotribenzoylmethane to diphenyl triketone benzoylphenylhydrazone has been investigated. For this purpose the *O*-phenylazo derivatives of *p*-nitrotribenzoylmethane, *p,p'*-dinitrotribenzoylmethane, *p*-methoxytribenzoylmethane and *p,p'*-dimethoxytribenzoylmethane were prepared and rearranged through the *C*-phenylazo isomer to the corresponding mixture of hydrazones which was then analyzed. The results show that a *p*-nitrobenzoyl migrates slower than benzoyl and *p*-methoxybenzoyl migrates at about the same rate as or somewhat faster than benzoyl. Evidence for the intramolecularity of the rearrangement has also been obtained.

Dimroth and Hartmann,<sup>2</sup> over 40 years ago, discovered a thermal rearrangement of phenylazotribenzoylmethane (Ia) to diphenyl triketone benzoylphenylhydrazone (IIa). Little attention has since been paid to this rearrangement. It was the purpose of the present work to examine the effect of *p*-substituents on the rearrangement by investigating the relative amounts of rearrangement products (II and III) obtained in the rearrangement of a series of *p*-substituted derivatives of I (Ib-e).



These azo compounds (Ib-e) were prepared by the method Dimroth and Hartmann had used for Ia.<sup>2</sup> Benzenediazonium chloride was allowed to react with the appropriate tribenzoylmethane to give the *O*-benzoylazo compound (IV) (Table I). In each case, the *O*-azo compound (IV) could be either of the compounds shown or be a mixture of the two. No attempt was made to investigate



this point. The *O*-azo compounds (IVb-e) were allowed to rearrange at 120°. Since the *C*-azo compounds (Ib-e) which are first formed<sup>2</sup> were difficult to isolate, they were allowed to rearrange in the reaction mixture in which they were prepared, directly to the hydrazones (IIb-e and IIIb-e). That the rearrangement of the *O*-azo compound (IV) proceeded through the *C*-azo compound (I) in every case was supported by the initial change of the yellow color of IV to the red color of I which then faded as the colorless hydrazone (II or III) was formed.<sup>3</sup> The ultraviolet spectra of Ia, IVd and IIIb were measured and are given in Figs. 1 and 2.

IVb gave a single rearrangement product in 84% yield. This substance was shown, as described in the following paper,<sup>4</sup> to be *p*-nitrophenyl triketone benzoylphenylhydrazone (IIIb)—formed

(1a) Taken from the Ph.D. thesis submitted by Charlotte S. Russell to Columbia University.

(1b) Department of Chemistry, University of Illinois, Urbana, Illinois.

(2) (a) O. Dimroth, *Ber.*, **40**, 2404 (1907); (b) O. Dimroth and M. Hartmann, *ibid.*, **40**, 4460 (1907); (c) O. Dimroth and M. Hartmann, *ibid.*, **41**, 4012 (1908).

(3) When the rearrangement of IVc was conducted at 120° side reactions leading to extensive decomposition to tars occurred. This compound was therefore heated at 75° until the color of the *C*-azo compound (Ic) had just begun to fade and the rearrangement was completed at 120°. It is of interest that this rearrangement apparently took place entirely in the solid state.

(4) D. Y. Curtin and C. S. Russell, *THIS JOURNAL*, **73**, Nov. (1951).

TABLE I

## O-Azo COMPOUNDS (IV)

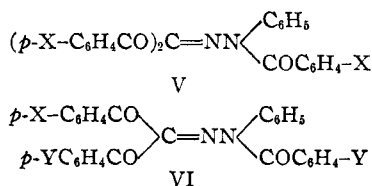
Prepared by the Reaction of Phenyl Diazonium Chloride with Tribenzoylmethane

O-Azo compound (IV)	Ketone employed	Yield of IV, %	M. p., °C. (dec.)	Analyses, %					
				Carbon		Hydrogen		Nitrogen	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
IVb	<i>p</i> -Nitrobenzoylmethane	85	65	70.4	70.4	4.0	4.2	8.8	9.1
IVc	<i>p,p'</i> -Dinitrotribenzoylmethane	60	90	64.4	64.8	3.5	4.0	10.7	10.2
IVd	<i>p</i> -Methoxytribenzoylmethane	65 <sup>a</sup> (33)	130	75.3	74.9	4.7	5.0	6.1	6.2
IVe	<i>p,p'</i> -Dimethoxytribenzoylmethane	50 <sup>a</sup> (60)	65	73.2	73.2	4.9	5.5	5.7	5.9

<sup>a</sup> Based on unrecovered starting material. The figure in parentheses is the amount of starting material recovered.

by migration of a benzoyl residue. IVc gave a 30% yield of each of the possible rearrangement products, IIc and IIId, which were separated by crystallization. The structural determination of these substances will be discussed in the following paper.<sup>4</sup> Although the total yield of hydrazones (IIc and IIId) was low we feel that no significant amount of either isomer was lost in the crystallization procedure but that the O-azo compound (IVc) undergoes an alternative decomposition to tarry by-products.

A careful search of the rearrangement products from IVb and IVc indicated that none of the other hydrazones (such as V and VI) which might have been formed by the interchange of X-C<sub>6</sub>H<sub>4</sub>CO-groups between molecules were present. This result suggests that the rearrangement is an intramolecular one.



In order to draw conclusions about the relative rates of migration of two groups by examining the relative amounts of the products formed, it was necessary to show that the products could not be interconverted under the reaction conditions. Both IIc and IIId were found to be unchanged after being heated at 120° for six hours.

The rearrangement of IVd gave an 86% yield of a mixture of hydrazones (IIId and IIId). Since attempts to separate the mixture were unsuccessful it was reduced with zinc and ammonia to a mixture of benzanilide and anisanilide. Chromatography of the anilide mixture gave a 75% yield (based on the hydrazone mixture) of benzanilide and 20% of anisanilide. Attempts to effect a more quantitative recovery of the anilides failed. In two other runs the reduction was carried out but, instead of the chromatographic separation of the anilides, the anilide mixture, after separation of other products by chromatography, was submitted for a carbon, hydrogen and methoxyl analysis. An overall 76% yield of the anilide mixture was obtained which consisted of 30% anisanilide and 70% benzanilide shown by this method.

The rearrangement of IVe gave a 93% yield of a mixture of hydrazones which was reduced to an anilide mixture (91% yield) as above. The carbon, hydrogen and methoxyl determination showed that the mixture consisted of 80% anisanilide and 20% benzanilide. Good agreement was obtained in

two completely independent rearrangement experiments.

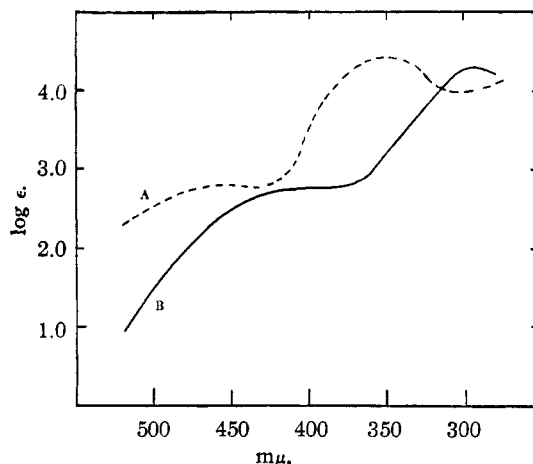


Fig. 1.—Spectra in benzene of (A) phenylazotribenzoylmethane (Ia) and (B) O-phenylazo-*p*-methoxytribenzoylmethane (IVd).

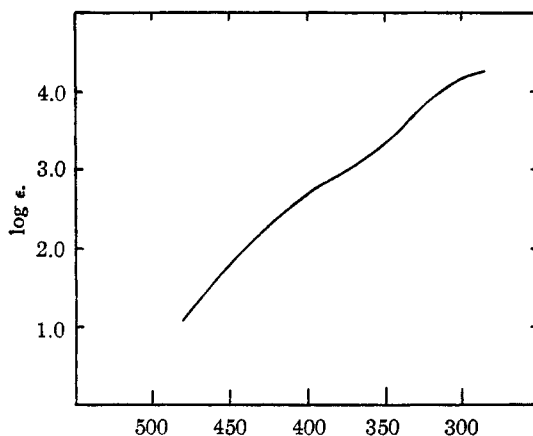


Fig. 2.—Spectrum in benzene of *p*-nitrophenyl phenyl triketone benzoylphenylhydrazone (IIIb).

The results above together with the calculated ratios of aroyl/benzoyl migration are summarized in Table II.

While these data yield no quantitative conclusions about the effect of substituents, they show that the competitive order of migration is *p*-anisoyl > benzoyl > *p*-nitrobenzoyl.

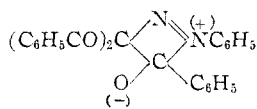
Although no unique mechanism for the rearrangement of I to II is indicated, the rearrangement would seem to be intramolecular as mentioned earlier. A mechanism in which the azo nitrogen attacks at a carbonyl carbon to give a transition state of which VII is an important resonance form

TABLE II

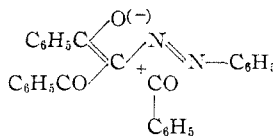
Compound rearranged	Yield of purified mixture, %	Benzoyl migration <sup>a</sup> , %	Aroyl migration <sup>a</sup> , %	Ratio: aroyl/benzoyl <sup>b</sup>
IVb	84	100	0	$p\text{-NO}_2/\text{H} = 0\text{--}0.4^c$
IVc	60	50	50	$p\text{-NO}_2/\text{H} = 0.5$
IVd	76	70	30	$p\text{-CH}_3\text{O}/\text{H} = 0.9^d$
IVe	90	20	80	$p\text{-CH}_3\text{O}/\text{H} = 2$

<sup>a</sup> In every case these results were duplicated in at least two independent experiments. <sup>b</sup> The appropriate statistical factor of two was applied in this calculation. <sup>c</sup> The value 0.4 is the maximum possible value and was obtained by making the assumption that all the product unaccounted for was the isomer formed by the migration of *p*-nitrobenzoyl. <sup>d</sup> To be consistent with the other results this value should be greater than 1. It is probably low because of the selective loss of anisilide during crystallization or chromatography. This substance is both more soluble and more strongly adsorbed on alumina than benzanilide. Loss of as much as 15% of the anisilide would have lowered the observed anisoyl/benzoyl ratio from 1.3 to 0.9.

appears to be excluded since the reverse effect of substituents is found for other reactions of this type such as the ammonolysis of *p*-substituted benzoic esters.<sup>5</sup>



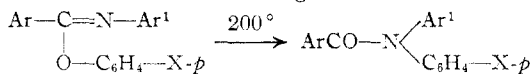
VII



VIII

The results are consistent with a mechanism with a transition state to which resonance form VIII is a significant contributor.<sup>6</sup>

This rearrangement seems to be related to certain other 1,3-rearrangements which, however, have been little investigated. Balfe and Kenyon<sup>7</sup> observed the uncatalyzed rearrangement of 4-hydroxy-2-hexene on three years of standing to 2-hydroxy-3-hexene with retention of optical activity. Recent work of Young, Hauser and co-workers<sup>8</sup> has provided evidence of a thermal rearrangement of  $\beta$ -diketone enol esters which is intramolecular as compared with the intermolecular acid-catalyzed rearrangement. The Chapman rearrangement<sup>9</sup> has been supposed to involve a similar intramolecular change.



### Experimental<sup>10</sup>

*p*-Nitrotribenzoylmethane was prepared by the method used by Claisen<sup>11</sup> for tribenzoylmethane. From 45 g. (0.20

(5) J. H. Gorvin, *J. Chem. Soc.*, 732 (1945).

(6) (a) For a discussion of the principles involved in reaching this conclusion see L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 184. (b) The transition state may lead directly to the product or there may be an intermediate ion pair of finite life of which VIII is the major contributor.

(7) M. P. Balfe and J. Kenyon, *Trans. Faraday Soc.*, **37**, 721 (1941); R. S. Airs, M. P. Balfe and J. Kenyon, *J. Chem. Soc.*, 18 (1942). A preliminary report of the demonstration of an intramolecular rearrangement of  $\alpha,\alpha$ -dimethylallyl chloride has been made by W. G. Young, S. Winstein and Harlan L. Goering, Abstracts of the 117th Meeting of the American Chemical Society, April, 1950, p. 70L.

(8) F. G. Young, F. C. Frostick, J. J. Sanderson and C. R. Hauser, *THIS JOURNAL*, **72**, 3635 (1950).

(9) A. W. Chapman, *J. Chem. Soc.*, 2426 (1930).

(10) All melting points are corrected. Analyses were carried out by the Clark Microanalytical Laboratories, Urbana, Illinois, and Dr. Francine Schwarzkopf, Elmhurst, New York.

(11) L. Claisen, *Ann.*, **291**, 25 (1896).

mole) of dibenzoylmethane and a 50% excess of sodium and *p*-nitrobenzoyl chloride was obtained 57 g. of a crude product which consisted of a mixture of *p*-nitrotribenzoylmethane and its *p*-nitrobenzoyl ester. The triketone was separated from its ester by aqueous extraction of a solution of the mixture which had been boiled in ethyl acetate with anhydrous potassium carbonate. The aqueous extract on acidification gave a 30% yield of *p*-nitrotribenzoylmethane, m.p. 161–201°. Because of the keto-enol equilibrium the melting point changed markedly with solvent. Recrystallization from 95% ethanol gave a constant m.p. of 182.5–185.5°. Recrystallization from acetone gave m.p. 161–182.7°.

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{15}\text{NO}_5$ : C, 70.8; H, 4.0; N, 3.8. Found: C, 70.5; H, 3.8; N, 4.0.

*p*-Nitrotribenzoylmethane in benzene could be converted to a copper derivative in essentially quantitative yield by treatment with cupric acetate (saturated aqueous solution).<sup>12</sup> Recrystallization from a chloroform-methanol mixture gave a m.p. of 259–261° (dec.) (sample placed in bath at 200°).

*Anal.* Calcd. for  $\text{C}_{44}\text{H}_{28}\text{CuN}_2\text{O}_{10}$ : C, 65.4; H, 3.5; Cu, 7.9. Found: C, 65.0; H, 4.1; Cu, 7.2.

The ethyl acetate solution mentioned above gave, on evaporation, a 70% yield of crude *p*-nitrotribenzoylmethane *p*-nitrobenzoate which on one recrystallization from acetone had a m.p. of 163–165°. Further recrystallization gave pale yellow needles, m.p. 166–167.5°.

*Anal.* Calcd. for  $\text{C}_{39}\text{H}_{18}\text{N}_2\text{O}_8$ : C, 66.7; H, 3.5; N, 5.3. Found: C, 66.9; H, 3.3; N, 5.7.

The ester could be hydrolyzed in 90% yield to *p*-nitrotribenzoylmethane with one hour of refluxing with 0.3 N sodium hydroxide.

*p,p'*-Dinitrotribenzoylmethane.—*p*-Nitrodibenzoylmethane was prepared by the method of Bülow and Hailer.<sup>13</sup> This method was used despite the low yield because of the availability of the starting material and the comparatively high purity of the product. Attempts to convert this substance to *p,p'*-dinitrotribenzoylmethane by a number of methods gave only starting material. The method below was finally employed. The diketone (30 g., 0.112 mole) was converted to the sodium salt by treatment with sodium ethoxide (prepared from 3 g., 0.130 mole, of sodium in 150 cc. of benzene) and 45 cc. of dry benzene. The sodium salt was collected and dried. It was then allowed to react with 19 g. (0.102 mole) of *p*-nitrobenzoyl chloride in 255 cc. of anhydrous ether at room temperature for 45 minutes. In addition to an 89% yield of crude starting material recovered by extraction with 700 cc. of hot ethanol, there was obtained 9.5 g. (15% yield) of *p,p'*-dinitrotribenzoylmethane *p*-nitrobenzoate, m.p. 179–182°. Further recrystallization from a mixture of benzene and ethanol gave white crystals, m.p. 180–182°.

*Anal.* Calcd. for  $\text{C}_{28}\text{H}_{17}\text{N}_3\text{O}_{10}$ : C, 61.4; H, 3.0; N, 7.4. Found: C, 62.1; H, 3.3; N, 7.4.

Hydrolysis of the ester (9.5 g., 0.0168 mole) was carried out by treating it with 10 g. (0.095 mole) of sodium carbonate and 4 cc. of water in 150 cc. of boiling ethyl acetate for three hours. Extraction with water and acidification with acetic acid gave a colorless solid. The product was suspended in ethanol, heated for 15 minutes and collected by filtration to give 6.0 g. (86% yield) of colorless *p,p'*-dinitrotribenzoylmethane, m.p. 168–170°. The triketone gave yellow solutions in ethanol and a yellow-orange color with 1% ferric chloride in 95% ethanol. Repeated recrystallization from ethanol gave a constant m.p. of 170–171°.

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{14}\text{N}_2\text{O}_7$ : C, 63.2; H, 3.4; N, 6.7. Found: C, 63.3; H, 3.0; N, 6.7.

A solution of the triketone in ethyl acetate, when shaken with saturated aqueous cupric acetate gave an olive green copper derivative, m.p. 282–287°, which did not, however, have a satisfactory analysis.

*p*-Methoxytribenzoylmethane was prepared from anisoyl chloride and dibenzoylmethane by the method of Claisen<sup>11</sup> for tribenzoylmethane. The solid triketone was isolated in 68% yield. After purification through its potassium salt, it gave a deep red color with ferric chloride solution and melted at 179–187°. Boiling in 95% ethanol (suspension)

(12) E. P. Kohler and R. Baltzly, *THIS JOURNAL*, **54**, 4015 (1932).

(13) C. Bülow and E. Hailer, *Ber.*, **35**, 915 (1902).

raised the m.p. 191–197°. The compound after repeated recrystallization from acetone had a m.p. of 205–207.5°, and gave the correct analysis for the triketone plus the elements of carbon dioxide.

*Anal.* Calcd. for  $C_{23}H_{18}O_4 \cdot CO_2$ : C, 71.6; H, 4.5. Found: C, 72.00; H, 4.7.

When the sample was dried under reduced pressure at 150° over phosphorus pentoxide for 11 hours the m.p. was still 206–206.8° but the analysis was correct for the triketone.

*Anal.* Calcd. for  $C_{23}H_{18}O_4$ : C, 77.1; H, 5.0;  $CH_3O$ , 8.7. Found: C, 76.8; H, 5.1;  $CH_3O$ , 8.5.

*p,p'*-Dimethoxytribenzoylmethane.—Dianisoylmethane was prepared by the method of Barnes, Goodwin and Cotten.<sup>14</sup> It was converted to *p,p'*-dimethoxytribenzoylmethane by the procedure of Claisen<sup>11</sup> for the unsubstituted triketone in 45% yield. This triketone was recrystallized from acetone and dried at 150° over phosphorus pentoxide for five hours. It melted at 209–210°.

*Anal.* Calcd. for  $C_{24}H_{20}O_5$ : C, 74.2; H, 5.2. Found: C, 74.2; H, 5.6.

The copper derivative was prepared in 92% yield by shaking a benzene solution with saturated aqueous cupric acetate for 30 hours. Recrystallization from a methanol-chloroform mixture gave a m.p. (dec.) of 245–247°.

*Anal.* Calcd. for  $C_{45}H_{38}CuO_{10}$ : C, 68.8; H, 4.6; Cu, 7.6. Found: C, 68.5; H, 5.0; Cu, 7.5.

**Preparation of the O-Phenylazo Compounds (Table I).**—The five triketones above were treated with benzene diazonium chloride under conditions which were essentially those of Dimroth and Hartmann for the unsubstituted compound.<sup>20</sup> The triketone was treated with twice the number of moles of potassium carbonate in 100 cc. of ethyl acetate/0.001 mole of triketone for times of 45–90 minutes. The potassium salt of the ketone was then extracted into cold water (in which certain of the salts were relatively insoluble) and the aqueous solution coupled with benzenediazonium chloride. Evaporation of the ethyl acetate solution above gave recovered starting material in some cases. The O-azo compounds were extracted into ether from their aqueous suspensions and then precipitated with petroleum ether (b.p. 30–60°). They were purified by precipitation from ether until the decomposition point remained constant. These compounds were all yellow but rearranged to the red C-azo compound when heated at the melting point.

**Rearrangement of O-Phenylazo-*p*-nitrotribenzoylmethane (IVb).**—When 1.80 g. (0.00380 mole) of IVb was heated at 120 ± 1° for six hours it melted to a red liquid which gradually solidified to a red solid which finally changed to light brown. Addition of 5 cc. of ethanol and filtration gave 1.6 g. of solid, m.p. 175–194°. Recrystallization from acetone yielded 1.51 g. (84%) of pale yellow needles, m.p. 199.5–203°. Concentration of the mother liquor gave only a red-brown tar. Further recrystallization of the product gave a m.p. of 201–203°. It was shown to be the *p*-nitrophenyl phenyl triketone benzoylphenylhydrazone (IIIb) by the method described in the following paper.<sup>4</sup>

*Anal.* Calcd. for  $C_{23}H_{19}N_3O_5$ : C, 70.4; H, 4.0; N, 8.8. Found: C, 70.3; H, 4.0; N, 9.2.

Other runs in which the time was shortened to as little as four hours gave the same product in the same yield.

**Rearrangement of O-Phenylazo-*p,p'*-dinitrotribenzoylmethane (IVc).**—When the reaction was carried out at an initial temperature of 120° extensive decomposition of the O-azo compound occurred. The rearrangement was therefore carried out by heating 0.425 g. (0.00810 mole) of IVc at 72–75° for six hours. The solid was then reddish-brown. The temperature was raised to 120° and after six hours the solid showed no signs of becoming lighter. It was triturated with cold 95% ethanol and filtered. The brown hydrazone mixture was heated in 60 cc. of acetone for five minutes. The acetone-insoluble fraction, di-*p*-nitrophenyl triketone benzoylphenylhydrazone (IIc), was collected and recrystallized from acetone. The colorless compound (0.117 g., 28% yield) melted at 253–258°. After recrystallization for analysis from acetone it melted at 257–258° (dec.). The structure is established in the succeeding paper.<sup>4</sup>

*Anal.* Calcd. for  $C_{28}H_{18}N_4O_7$ : C, 64.4; H, 3.5; N, 10.7. Found: C, 64.2; H, 3.9; N, 10.7.

(14) R. P. Barnes, T. C. Goodwin and T. W. Cotten, *THIS JOURNAL*, **69**, 3135 (1947).

Concentration of the acetone filtrates above and crystallization of the resulting solid from benzene yielded 0.134 g. (32%) of phenyl *p*-nitrophenyl triketone *p*-nitrobenzoylphenylhydrazone (IIIc). The structure is established in the following paper.<sup>4</sup> In another similar reaction a yield of 30% each of IIc and IIIc was obtained.

*Anal.* Calcd. for  $C_{28}H_{18}N_4O_7$ : C, 64.4; H, 3.5; N, 10.7. Found: C, 64.5; H, 4.1; N, 10.2.

IIc and IIIc could be recovered completely unchanged after being heated at 120° for six hours.

**Rearrangement of O-Phenylazo-*p*-methoxytribenzoylmethane (IVd).**—IVd 4.94 g. (0.011 mole) rearranged at 120 ± 1° to a clear orange-yellow liquid in five hours. The glass obtained on cooling was made to crystallize by scratching with benzene. After filtration, 4.2 g. (86%) of the mixture of IIId and IIId, m.p. 113–161°, was obtained. Repeated recrystallization from alcohol gave a constant m.p. of 140–154°.

*Anal.* Calcd. for  $C_{23}H_{22}N_2O_4$ : C, 75.3; H, 4.8; N, 6.1. Found: C, 75.4; H, 4.8; N, 6.0.

Since the two hydrazones (IIId and IIId) could not be separated by crystallization or chromatography on silicic acid, the mixture (1.03 g., 0.00200 mole) was reduced with zinc dust (1 g., 0.015 g.-atom) and ammonia (4.7 cc.) in 30 cc. of ethanol to a mixture of anisilide and benzanilide by the method of Dimroth and Hartmann.<sup>20</sup> After removal of excess zinc, distillation of the solvent and extraction of basic side-products with 40 cc. of 3 *N* hydrochloric acid, 0.57 g. of crude product was obtained. A 0.100-g. aliquot in 10 cc. of benzene was adsorbed on Eimer and Amend 80–200 mesh alumina activated at 300°. Elution with 1% acetone in benzene gave 0.038 g. (equivalent to a 55% yield in the reduction) of benzanilide, m.p. 162–163°, and 0.016 g. (equivalent to a yield of 20% in the reduction) of anisilide, m.p. 167–170°. Other methods of separating the mixture of anilides such as fractional sublimation, steam distillation or selective formation of anisilide picrate failed.

In another similar reduction the crude anilide mixture was separated from the other products by adsorption on a column of alumina as above and elution with 1% acetone in dry benzene until no more solid was obtained. The total solid amounted to 76%. Two methoxyl determinations gave an average value of 4.0 which corresponds to a mixture containing 29% anisilide and 71% benzanilide.<sup>15</sup> The two sets of values given below were obtained from two different reaction mixtures.

*Anal.* Calcd. for 29% anisilide and 71% benzanilide: C, 77.7; H, 5.7;  $CH_3O$ , 4.0. Found: C, 77.8, 78.0; H, 5.6, 5.9;  $CH_3O$ , 4.3, 3.6.

**Rearrangement of O-Phenylazo-*p,p'*-dimethoxytribenzoylmethane (IVe).**—The rearrangement of IVE (5.36 g., 0.011 mole), when carried out as described above gave a total of 4.97 g., m.p. 130–140°, of a mixture of hydrazones IIe and IIIE. Recrystallization from ethanol gave a constant m.p. of 134–142°.

*Anal.* Calcd. for  $C_{30}H_{24}N_2O_6$ : C, 73.2; H, 4.9; N, 5.7. Found: C, 73.2; H, 5.0; N, 5.8.

Attempts at separating the hydrazone mixture by chromatography on silicic acid were unsuccessful.

The mixture was therefore reduced as above to give a 91% yield of an anilide mixture, m.p. 120–155°, after purification by chromatography. Analyses of the mixtures from two different reductions gave values corresponding to the calculated values for a mixture 82% anisilide and 18% benzanilide.<sup>16</sup>

*Anal.* Calcd. for 82% anisilide and 18% benzanilide: C, 75.2; H, 5.7;  $CH_3O$ , 11.2. Found: C, 75.5, 75.7; H, 6.0, 6.0;  $CH_3O$ , 11.2, 11.6.

The ultraviolet spectra were obtained with a Beckman DU quartz spectrophotometer with a hydrogen arc from 270–320 mμ and a tungsten lamp at higher wave lengths. The spectra were measured in dry benzene. The concentrations were: Ia, 0.00014; IVd, 0.00058, IIId, 0.00013 *N*. Ia was prepared by the method of Dimroth and Hartmann.<sup>20</sup> IVd was employed because it was more stable than the other O-azo compounds.

NEW YORK 27, N. Y.

RECEIVED APRIL 9, 1951

(15) A methoxyl value of 4.0 ± 0.3% corresponds to a mixture containing 29 ± 3% of anisilide.

(16) A methoxy value of 11.4 ± 0.3 corresponds to a mixture containing 83 ± 3% anisilide.