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.]

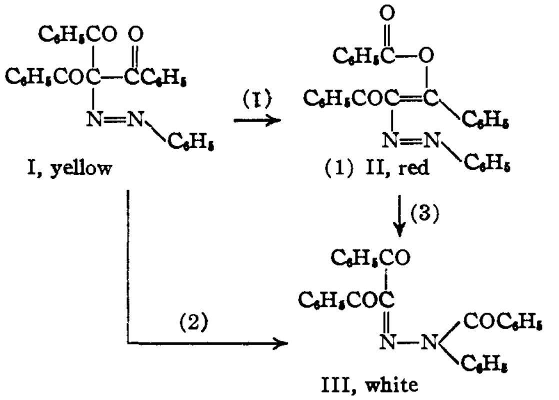
Rearrangements of Benzeneazotribenzoylmethane.[1] 1,3-Benzoyl Migrations from Carbon to Oxygen and from Carbon to Nitrogen

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.



I, yellow

II, red

III, white

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

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[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).

TABLE I

RATES OF REARRANGEMENT OF BENZENEAZOTRIBENZOYLMETHANE (I) AND ENOL BENZOATE II IN DIOXANE SOLUTION

T, $\pm 0.02°$	$10^5 (k_1 + k_2)$, (sec.$^{-1}$)	f_e $[k_1/(k_1 + k_2)]$	$10^5 k_1$, sec.$^{-1}$	$10^5 k_2$, sec.$^{-1}$	$10^6 k_3$, sec.$^{-1}$
58.80[a]	3.40[a]	0.493[a]	1.67[a]	1.72[a]	..
68.73	10.73	.481	5.16	5.57	..
77.42	25.5	.480	12.2	13.3	..
97.10	..	..	(82)[b]	(90)[b]	1.48

E_a 25.1 ± 0.6 kcal./mole, $S^{\ddagger}$ −7.0 ± 1.5 e.u.

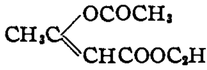
[a] Average of three determinations. [b] Extrapolated from values at 77.42°.

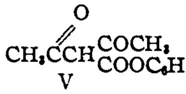
give the first-order constants for the formation of II and III reported in Table I.

It will be noted that the fractions of path 1 and path 2 (f_e and f_h) are quite insensitive to variation of the temperature over the range employed. The rearrangement of enol benzoate II to hydrazone III was followed in dioxane at 97.10° and found to be first order also with the rate constant (k_3) shown in Table I. The relative values $k_1:k_2:k_3$ at that temperature are thus 55:60:1.

An attempt to study the effect of ionizing solvents on the rearrangements of the yellow azo compound I to the products II and III was complicated by a competing reaction. Thus, in aqueous dioxane containing even a few per cent of water, compound I ionized to benzenediazonium ion which lost nitrogen irreversibly or could be coupled with β-naphthol or R salt as will be discussed later in this paper. At least, then, the rearrangements must be much less sensitive to solvent ionizing power than is diazonium ion formation. An estimate of the sensitivity of k_3 to solvent ionizing power was made by carrying out the rearrangement of the enol benzoate II to the hydrazone III in dioxane–water (80:20) at 97.1°. The estimated maximum value of the rate constant (2.3×10^{-5} sec.$^{-1}$) suggests that the value of "*a*"[6,7] is 0.1 or less.[8] Data on the sensitivity of allylic rearrangements to solvent ionizing power have been summarized by Smith[7] and found to fall into two categories. Those which isomerize by way of ions have "*a*" values of 0.5 or greater; those presumed to proceed by a molecular mechanism (through a transition state with relatively little charge separation) have "*a*" values of 0.15 or less. The rearrangement of II to III clearly belongs in the class of reactions characterized by low sensitivity to solvent ionizing power.

A further conclusion can be drawn from the rearrangement of the enol benzoate II to the hydrazone III in aqueous dioxane. Since the azo triketone I was shown, as will be discussed later, to react rapidly even at 25° in this medium to give benzenediazonium ion or its further reaction products, the conversion of II to III must occur directly (at least for the most part) and not by way of I. If the direct rearrangement of II to III is faster than return to I, that is $k_3 > k_{-1}$, then, since the equilibrium constant K for the equilibrium between triketone I and enol benzoate II is k_1/k_{-1} and since $k_1/k_3 = 55$ it follows that $K > 55$ or that the enol benzoate II is more stable than the triketone I by at least 3 kcal./mole ($\Delta F^0_1 \leq -3$).[12] That the equilibrium should lie toward the enol benzoate II deserves comment since in known interconversions of ketone and enol ester the equilibrium lies in the opposite direction. For example, the enol acetate IV of ethyl acetoacetate was found[14] to rearrange at 240° to the diketo ester V and the enol acetates VI of acetone (R = CH_3) and acetophenone (R = C_6H_5) have been found[14,15] to rearrange to the β-diketones VII at 500°. The steric crowding in the tribenzoyl compound I which is partially relieved on rearrangement is apparently responsible to a large extent for the predominance of the enol benzoate. It is probably significant in this connection that of the benzeneazotriketones and keto esters which have been rearranged, only the triaroylketones have been shown to give the enol ester.


IV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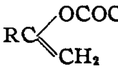
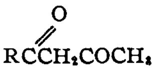

VI


VII

In an investigation of substituent effects, p-methoxy-, p-nitro- and 2,4,6-trichloro-benzeneazotribenzoylmethane (VIII), (IX) and (X) were prepared and their rearrangements in dioxane at 58.80° studied by the methods described for the unsubstituted azo compound I. The results are summarized in Table II.

$$(C_6H_5CO)_3CN{=}NAr$$

VIII, Ar = p-$CH_3OC_6H_4$–
IX, Ar = p-$NO_2C_6H_4$–
X, Ar = 2,4,6-$Cl_3C_6H_2$–

The significance of the facts just presented with respect to the mechanisms of the three types of benzoyl migrations can now be discussed. At

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(6) S. G. Smith, A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).

(7) S. G. Smith, *ibid.*, **83**, 4285 (1961).

(8) Unfortunately no Y[9] or Z[10] value is available for dioxane. An estimate using the equation of Fainberg and Winstein[11] (Y−5.64) combined with the *m* value of 0.560 for aqueous dioxane[6] gives 2.7 for the difference in the log *k*'s of the solvolysis of p-methoxyneophyl toluenesulfonate in dioxane and dioxane–water (80:20). This together with the rate constants for the rearrangement of II to III (k_3) reported in this paper gives 0.07 for "*a*."[9] Other methods of making the estimate involving extrapolation of *Z* values[10] to pure dioxane or extrapolation of the log *k* *vs.* $(D - 1)/(2D + 1)$ plot[9] give similar results.

(9) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948); S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

(10) E. M. Kosower, *ibid.*, **80**, 3253 (1958).

(11) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

(12) Symmetry considerations can account for as much as 0.7 kcal. of the total. Thus, if the symmetry number σ is 3 for the triketone I, $-RT \ln \sigma$ is 0.72 kcal. (A value of 1 for the symmetry number of the enol benzoate gives $RT \ln \sigma = 0$.)[13]

(13) G. J. Janz, "Estimation of Thermodynamic Properties of Organic Compounds," Academic Press, Inc., New York, N. Y., 1958, pp. 17 ff.

(14) W. Wislicenus and H. Körber, *Ber.*, **34**, 218 (1901); **38**, 546 (1905).

(15) A. B. Boese, Jr., and F. G. Young, Jr., U. S. Patent 2,395,280 [*C. A.*, **40**, P3130[8] (1946)]; R. J. P. Allan, J. McGee and P. D. Ritchie, *J. Chem. Soc.*, 4700 (1957). The resemblance of these 1,3-migrations to the rearrangement of N-nitrosoamides [H. Zollinger, "Diazo and Azo Chemistry," Interscience Publishers, New York, N. Y., 1961, p. 153 ff.] may also be noted.

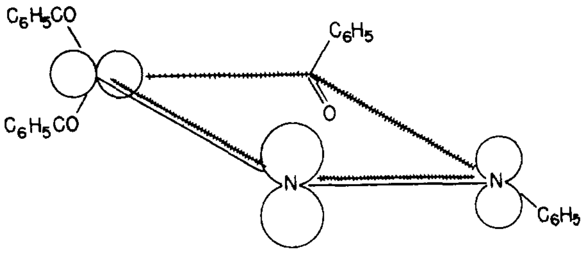


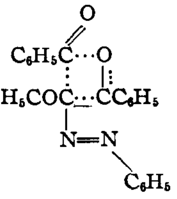
Figure 1.

least three categories of mechanism need to be considered. The rearrangements could proceed as independent molecular reactions without the necessity of any intermediate as was proposed earlier[4] for the rearrangement of azotriketone I to hydrazone III and also for the formation of ketones from enol esters.[15] In the first approximation the transition states of such rearrangements can be represented by the structures below and are reached without the necessity of serious alteration of the charge distribution in the initial molecule.

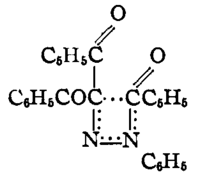
TABLE II

RELATIVE RATES OF REARRANGEMENT OF THE SUBSTITUTED BENZENEAZOTRIBENZOYLMETHANES I, VIII, IX, AND X AND THE RELATED ENOL BENZOATES IN DIOXANE SOLUTION

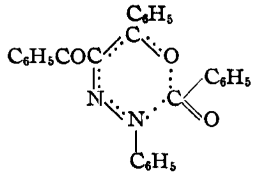
Benzeneazo substituents	f_e	k_{obs} (rel.)	k_1 (rel.) 58.80°	k_2 (rel.)	k_3 (rel.) 97.10°
p-OCH_3 (VIII)	0.357	0.44	0.32	0.56	0.79
None (I)	.493	(1.00)	(1.00)	(1.00)	(1.00)
p-NO_2 (IX)	.592	20	24	17	12
2,4,6-Cl_3 (X)	.825	26	44	9	...



‡I → II

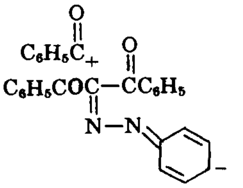


‡I → III



‡II → III

The observed substituent effects can be accommodated (somewhat arbitrarily) by the inclusion of dipolar resonance structures as, for example, XI in the description of the transition state ‡I→II.



XI

$$\begin{tikzcd} A \arrow[rr, "k_1"] \arrow[dr, "k_2"'] & & E \arrow[dl, "k_3"] \\ & H & \end{tikzcd}$$

If the azo triketone (I or its substituted derivative) is represented by A, the enol benzoate (II or its derivative) by E and the benzoylhydrazone (III or its derivative) by H the kinetic scheme is that shown where the k's have the significance given them in the early part of this paper. Such a rearrangement is somewhat reminiscent of the ready acyl migration characteristic of acyl amino alcohols[16] and amino phenols.[17] Intramolecular 1,3-shifts are not very common, however, and of a variety of possible candidates examined critically by Wiberg, Rowland, Shryne and Kintner[18] only the rearrangement at 250° of phenyl N-phenylbenzimidate to N-phenylbenzanilide appeared to be intramolecular, the remainder being, apparently, radical chain reactions. Although the four- and six-center molecular mechanisms cannot be ruled out absolutely by the available evidence, several considerations make them seem unattractive. It will be recalled that the rearrangements of azotriketone I both to the enol benzoate II and to the hydrazone III (which would involve four-membered cyclic transition states) were some 50 times as fast as the rearrangement of II to III which has available a six-membered transition state. Such behavior is contrary to that found in other ring closures[19] and there do not seem to be special features in the reactions discussed here to make it seem reasonable. In fact, a detailed consideration of the stereoelectronics of the molecular mechanism gives quite the contrary result. The relevant features are illustrated in Fig. 1 for the carbon-to-nitrogen rearrangement 2. It will be seen that the p-orbital being developed on the carbon atom from which the migrating benzoyl group is departing is being developed in the plane of the four-membered ring which minimizes overlap with the adjacent p-orbital on the central nitrogen atom. In other words, resonance interaction of the C⋯N⋯N system is sterically inhibited by the constraint imposed by the four-membered ring being formed. A very similar situation exists in the carbon-to-oxygen rearrangement 1 but not in the oxygen-to-nitrogen rearrangement which could involve a six-membered ring with quite different stereochemistry.

Further objections to the set of molecular mechanisms are discovered on closer examination of the substituent effects. As was mentioned, the observed effects can be explained by the arbitrary inclusion of selected resonance structures in the transition state. However, the transition states for the rearrangements from I and II to hydrazone III might have been expected to have an important contribution from resonance forms such as that shown below. The suggested increase in positive charge on the azo nitrogen atom in going to the transition state would predict that the reaction should be aided by a $-\sigma$, contrary to the observed results. Finally, and perhaps most significantly, it may be noted that the rearrangement of azo-

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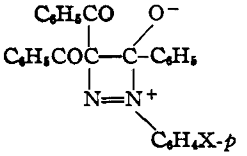
[16] See for example, L. Welsh, *J. Am. Chem. Soc.*, **69**, 128 (1947).

[17] See W. J. Hickinbottom, "Chemistry of Carbon Compounds," Vol. IIIA, Edited by E. H. Rodd, Elsevier Publishing Co., Amsterdam, 1954, pp. 450 ff.

[18] See K. B. Wiberg, T. M. Shryne and R. Roy Kintner, *J. Am. Chem. Soc.*, **79**, 3160 (1957); K. B. Wiberg and B. I. Rowland, *ibid.*, **77**, 2205 (1955).

[19] See G. W. Wheland, "Advanced Organic Chemistry," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 484 ff.



triketone I to the enol benzoate involves no change in the bonding of the —N=NC_6H_4X portion of the molecule. The other two rearrangements leading to the hydrazone both involve a change in the hybridization at the nitrogen atom *para* to the substituent. It seems quite unreasonable, then, that changes in the substituent should have their greatest effect on the rate of the azotriketone–enol benzoate rearrangement, the rearrangement farthest from the substituent.

This evidence, though not compelling, suggests strongly that the reaction is more complicated that is indicated by the scheme above and that there is, in fact, an intermediate, either a pair of free radicals or an "ion pair," possibly with the two "ions" held together tightly with a rather strong π-bond[20] or as a charge transfer complex.[21] The picture then becomes that shown below. If it is accepted for reasons advanced earlier in this paper that E rearranges to H without returning to A, *i.e.* that $k_{-e} + k_{-h} >> k_{-i}$, application of the steady state approximation to the rearrangement of A to the mixture of E and H under the conditions (at 58.8°) where rearrangement of E to H is negligible [*i.e.*, $k_{-e}(E) << k_i(A)$] gives

$$\mathrm{A} \underset{k_{-i}}{\overset{k_i}{\rightleftarrows}} \mathrm{In} \begin{cases} \underset{k_{-e}}{\overset{k_e}{\rightleftarrows}} \mathrm{E} \\ \underset{k_{-h}}{\overset{k_h}{\rightleftarrows}} \mathrm{H} \end{cases}$$

$$-\mathrm{d}A/\mathrm{d}t = k_i(\mathrm{A});\ \mathrm{d}E/\mathrm{d}t = f_e k_i(\mathrm{A});\ \mathrm{d}H/\mathrm{d}t = f_h k_i(\mathrm{A})$$

$$\text{where } f_e = k_e/(k_e + k_h) \text{ and } f_h = k_h/(k_e + k_h)$$

It is seen that k_1 and k_2 calculated above are not pure rate constants but products of rate constants times the fractions f_e and f_h which describe the collective fate of the species In. If this treatment is correct a plot of the logarithm of the rate constant for the disappearance of A (*i.e.*, log k_{obs} = log k_i) against σ should lead to a linear Hammett plot[22] whereas the plot of log k_1 or log k_2 against σ should only be linear provided f_e and f_h are independent of the substituent changes which they are not as can be seen in Table II. Although the data are limited it may be noted that a plot[22] of log k_{obs} against σ leads to a line with a slope and probable error given by the method of least squares[23] $\rho = +1.60 \pm 0.03$. Analysis of the k_3's is also possible in terms of a kinetic scheme assuming the intervention of the intermediate. Since f_e and f_h are shown by the data in Table I to be quite insensitive to an increase in temperature in the reactions of the parent compound I, it will be assumed that the values employed for the *p*-methoxy and *p*-nitro derivatives at 97° are approximately the same as the respective values at 58°. The steady state treatment of the rearrangement of the enol benzoates to the benzoylhydrazones leads to the equation

$$\mathrm{d(H)}/\mathrm{d}t = k_{-e} f_h(\mathrm{E})$$

from which it follows that the measured rate constant, k_3, is equal to $k_{-e}f_h$ and $k_{-e} = k_3/f_h$. A plot of log $(k_3/f)_h$ gives an excellent straight line with a slope, $\rho = 0.840 \pm 0.008$, but with the σ^- value of +1.27 employed as the substituent constant for the nitro group.[22] A free radical or ionic reaction of the type proposed for the formation of the intermediate from either azotriketone A or enol ester E could reasonable by expected to correlate with σ^- or with a value of σ intermediate between σ and σ^-.[24,25] It might be hoped that such a treatment of the data would make possible a choice between the two kinetic situations, one with, and one without an intermediate. Unfortunately the paucity of data available and the difficulties[24] inherent in the choice of the correct values for the σ to be employed make such a choice impossible. Thus, plots of log k_1 against σ, and log k_2 and log k_3 against σ^- lead to reasonable linear plots with $\rho_1 = 1.79 \pm 0.02$, ρ_2 0.956 ± 0.002 and $\rho_3 = 0.73 \pm 0.04$. A further basis for a choice between a molecular mechanism or radical mechanism on the one hand and an ionic mechanism on the other might seem to arise from a consideration of the magnitudes of the ρ's and the need (or lack of need) for augmented values of σ (σ^+ or σ^-). In fact, the value of 1.79 for ρ_1 appears large for a molecular mechanism in any case and particularly so for a change of substituent at a site so remote from the reaction area. Unfortunately not only ionic reactions but also reactions believed to proceed by a molecular or a free radical mechanism have been shown to be correlated with an augmented value of σ (σ^+).[26] Furthermore both free radical and molecular reactions have been found to be subject to substantial polar effects.[26]

Although the arguments presented provide evidence for an intermediate, verification of its

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[20] M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford Press, London, 1949, pp. 17,18.

[21] See A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 199, 200.

[22] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 184 ff. Sigma constants employed here were those cited by R. W. Taft, N. C. Deno and P. Skell, *Ann. Rev. Phys. Chem.*, **9**, 292 (1958).

[23] L. P. Hammett, "Introduction to the Study of Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1952, pp. 410, 411.

[24] H. van Bekkum, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959). See also J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 88 ff.

[25] In view of the limited data it is not felt that the "linearity" of the plot of log k_i against σ for the *p*-nitro substituent on the one hand and of log k_{-e} against σ^- on the other has significance. In fact, the linearity of the plot of log k_i is optimized when a value of σ for the *p*-nitro-substituent of 0.94, intermediate between σ of +0.79 and σ^- of 1.27 is employed. In this case $\rho = 1.38$.

[26] The Claisen rearrangement (which may be taken as one of the reactions most likely to proceed by a molecular mechanism) has ρ values of only −0.4-(−)0.7 but the data are best correlated with σ^+ [W. N. White, D. Gwynn, R. Schlitt, C. Girard and W. Fife, *J. Am. Chem. Soc.*, **80**, 3271 (1958); H. L. Goering and R. R. Jacobson, *ibid.*, **80**, 3277 (1958); W. N. White and W. K. Fife, *ibid.*, **83**, 3846 (1961)]. Wiberg and Rowland[18] found a value of $\rho = 1.75$ for the effect of substituents attached directly to the migrating phenyl ring in the rearrangements of substituted phenyl N-phenylbenzimidates. Free radical processes have been shown to have ρ's with absolute values as large as 1.5 [see G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958); E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 394 (1960)] and to be best correlated with an augmented value of σ, in this case σ^+.

existence and a detailed description of its structure must await further investigation. It seems unlikely that free radicals easily interceptible by oxygen are involved since the rearrangements show no particular sensitivity to the presence of air. It is of interest, however, that in a preliminary experiment[27] the solid azotriketone I, when heated to the point where rearrangement began as indicated by a change in color, showed an electron spin resonance signal which was absent either in the solid at lower temperatures or in the melt. What the responsible radicals are and what part, if any, they play in the rearrangements under consideration remains to be discovered.[28]

The observation that the rearrangement of azotriketone I to the mixture of II and III occurs when the solid is heated and without appreciable melting prompted an examination of the product ratio when the reaction was carried out in this way. Analysis of the products of the two reactions carried out to about 75% conversion by heating the solid at 95–105° gave for the fraction, f_e, of enol benzoate values of 0.69 and 0.76 with an average of 0.73. A similar reaction, allowed to melt, gave for the same fraction a value of 0.51 as compared with the value of 0.49 for the reaction in dioxane solution. Microscopic examination of crystals of I, both freshly crystallized and after standing for some time, showed that they were undergoing a change which was accelerated when they were suspended in mineral oil. It has since been discovered[29] that the freshly crystallized substance contains ether of crystallization which had diffused out with a certain amount of disruption of the crystal structure of the sample which was allowed to rearrange. A study of the reactions in the solid state is being continued. It is hoped that an extension of these results may contribute to the development of a relatively new area of chemistry. By carrying out reactions in the solid state with the molecules oriented in a rigid matrix it has been possible to gain additional control of reaction rates, and hence of products.[30,31,32]

Incidental to the study reported in the first part of this paper, the coupling reactions with β-naphthol, β-naphthylamine and disodium 2-naphthol-3,6-disulfonate or "R salt" were examined. A set of reactions was carried out in 85% aqueous dioxane with an initial concentration of azotriketone I of from 1.14×10^{-5} to 5.69×10^{-5} and with amounts of coupling agent varying from an equimolar amount to nearly an 11,000-fold excess. In the runs with only a ten-fold excess of β-naphthol or β-naphthylamine as coupling agents a plot based on the assumption the reaction was first order in azotriketone and zero order in coupling agent showed downward curvature. As the initial amount of amine or naphthol was increased the plots became straighter and with a 1070-fold excess of β-naphthol of a 4800-fold excess of β-naphthylamine linear first-order plots were obtained with rate constants which appeared to be converging to the same approximate value. The data are summarized in Table III.

TABLE III

RATE CONSTANTS FOR THE COUPLING OF BENZENEAZOTRIBENZOYLMETHANE (I) WITH β-NAPHTHYLAMINE AND β-NAPHTHOL IN DIOXANE-WATER (85.15) AT 26.5 ± 0.5°

β-Naphthol		β-Naphthylamine	
Ratio of naphthol to I	$10^4 k_1$, sec.$^{-1}$	Ratio of amine to I	$10^4 k_1$, sec.$^{-1}$
11.2	$6.1^{a,b}$	480	2.2^{b}
112	$8.4^{a,b}$	1000	5.5^{b}
1070	12.68 ± 0.07	2000	7.7^{b}
10700	13.84 ± 0.06	4800	11.05 ± 0.04

[a] Measured at 25.0 ± 0.5°. [b] Value of the initial slope since the plot was not linear.

It seems clear that the process being measured is primarily the dissociation of the benzeneazotriketone I to benzenediazonium ion and tribenzoylmethane anion. The failure of the "limiting" rate constants to agree better is hardly surprising in

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

view of the difference in media in the two sets of reactions and, in particular, the possibility of ion pairing and also an acid-catalyzed side reaction leading to tribenzoylmethane and the diazonium ion when β-naphthol is present. R salt was more effective as a coupling agent since even a tenfold excess gave a linear first-order plot with a rate constant which was independent of the concentration of R salt. The value of $16.70 \pm 0.04 \times 10^{-4}$ sec.$^{-1}$ of the first-order constant at 28.0 ± 0.5° was only slightly higher than the "limiting values" found with β-naphthol and β-naphthylamine in Table III. The sensitivity of the coupling was shown by the observation that it was extremely slow in pure dioxane but increased rapidly with the addition of water; an increase in the % water from 12 to 50 increased the rate by a factor of about 3.5 at 27°.

Experimental[33]

p-Methoxybenzeneazotribenzoylmethane (VIII) was prepared from p-methoxybenzenediazonium fluoroborate and the potassium salt of tribenzoylmethane by the method employed[6] for the unsubstituted compound I. Crystallization from dioxane–hexane (between 25° and 0°) gave 36% of VIII based on the 61% of unrecovered tribenzoylmethane. The yellow solid had m.p. 140° dec. and gave a red color with 2-naphthol in ethanol. The sample prepared for

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(27) Unpublished work of Mr. Larry Miller and Mr. R. A. Meinzer. We are indebted to Professor H. S. Gutowsky and Mr. R. A. Meinzer for providing facilities and assistance with the e.s.r. study.

(28) Attempts to initiate the rearrangements of benzeneazotribenzoylmethane by irradiation with a sun lamp showed almost no effect after 10 hours at 25°.

(29) Unpublished work of Mr. Larry Miller.

(30) See H. I. Bernstein and W. C. Quimby, *J. Am. Chem. Soc.*, **65**, 1845 (1943).

(31) T. Sadeh and G. M. J. Schmidt, *ibid.*, **84**, 3970 (1962), and references cited therein.

(32) J. F. Brown, Jr., and D. M. White, *ibid.*, **82**, 5671 (1960); D. M. White, *ibid.*, **82**, 5678 (1960); see J. F. Brown, Jr., *Scientific American*, **207**, 82 (1962).

(33) 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. Chlorine analyses were performed by the Clark Microanalytical Laboratories. 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 HR60 spectrophotometer. Spectra are reported in τ units.[34] 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,[1] from Univ. Microfilms, Ann Arbor, Mich.

(34) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

analysis was crystallized from ether. The infrared spectrum in methylene chloride had strong absorption at 1672 with an inflection at 1700 and a less intense sharp absorption at 1597 cm.$^{-1}$. The ultraviolet-visible spectrum in dioxane had λ_{max} 248 (ϵ 31,700), 324 (ϵ 17,300) and 416 mμ (ϵ 557).

Anal. Calcd. for $C_{29}H_{22}N_2O_4$: C, 75.3; H, 4.8; N, 6.1. Found: C, 75.0; H, 4.8; N, 6.6.

α-*p*-Methoxybenzeneazo-β-benzoyloxybenzalacetophenone.—The *p*-methoxyazotriketone VIII (293 mg.) in 2 ml. of dioxane was heated at 100° for 1 hr. Evaporation of the solvent under reduced pressure and at a temperature less than 30° gave a red residue which was purified by chromatography over 32 g. of Florisil packed in hexane. A red band eluted by benzene gave a residue crystallized from dioxane–hexane (25–0°). There was obtained a mixture of red and yellow crystals which was separated mechanically to give 15.7 mg. of red crystals, 15.5 mg. of yellow and 11.3 mg. of mixture of crystals too small to separate. Both the red and yellow forms melted at 145° dec. and showed similar infrared spectra. Crystallization of the yellow form from acetone (25–0°) gave a mixture of the red and yellow. The red form was crystallized from acetone to give an analytical sample, m.p. 145.2–146.3°, when introduced into the m.p. bath at 142° and heated at 2°/min. The infrared spectrum in methylene chloride showed strong absorption at 1747, 1678 and 1603 cm.$^{-1}$. The ultraviolet spectrum in dioxane showed λ_{max} 243 mμ (ϵ 34,900) and 373 mμ (ϵ 28,900) with no maximum but only end absorption in the visible region.

Anal. Calcd. for $C_{29}H_{22}O_4$: C, 75.3; H, 4.8; N, 6.1. Found: C, 74.8; H, 4.9; N, 6.1.

Diphenyltriketone *sym*-Benzoyl-*p*-methoxyphenylhydrazone.—The *p*-methoxyazotriketone VIII (115 mg.) was heated at 125° for 13 hr. to give 110 mg. of pale yellow residue which when crystallized from methanol amounted to 41 mg. of hydrazone, m.p. 193–194°. Further recrystallization from methanol gave m.p. 199–200°. The ultraviolet spectrum in dioxane showed λ_{max} 228 mμ (ϵ 24,800) and 262 mμ (ϵ 26,400) with end absorption in the visible region as far as 470 mμ.

Anal. Calcd. for $C_{29}H_{22}N_2O_4$: C, 75.3; H, 4.8; N, 6.1. Found: C, 75.5; H, 4.8; N, 6.4.

***p*-Nitrobenzeneazotribenzoylmethane (IX).**—Tribenzoylmethane (2.0 g.) was converted to the potassium salt as with the parent compound I and coupled with diazonium chloride solution from 552 mg. (4.0 mmoles) of *p*-nitroaniline in 4 ml. of 20% hydrochloric acid and 276 mg. (4.0 mmoles) of sodium nitrite in 1 ml. of water at 0° followed by addition of 10 ml. of cold 4 *M* potassium acetate. Tribenzoylmethane (1.0 g.) was recovered from the preparation of its salt. The coupling product was obtained by decantation of the liquid from the red gum which had formed after 5 min. The gum, taken up in ether, dried and hexane added, gave 825 mg. of bright orange azotriketone (IX), which softened and turned red at 110° but resolidified above 140° before remelting at 195°. It was purified by recrystallization from ether (25–0°). The infrared spectrum in methylene chloride solution had absorption at 1679, 1700 (inflection), 1600, 1535 and 1354 cm.$^{-1}$,

Anal. Calcd. for $C_{28}H_{19}N_3O_5$: C, 70.4; H, 4.0; N, 8.8. Found: C, 70.9; H, 4.0; N, 8.7.

α-*p*-Nitrobenzeneazo-β-benzoyloxybenzalacetophenone (125 mg., m.p. 175–175.5° when introduced into the bath at 173° and heated at 2°/min.) was prepared from 500 mg. of nitroazotriketone IX in 3 ml. of dioxane at 100° for 0.5 hr. followed by evaporation of the solvent and chromatography of the red residue over 35 g. of Florisil packed in hexane (elution with 1:3 methylene chloride–hexane). The infrared spectrum in methylene chloride had absorption at 1742, 1680, 1613, 1525 and 1350 cm.$^{-1}$. The ultraviolet spectra in dioxane had λ_{max} 237 mμ (ϵ 32,400) and 368 mμ (ϵ 25,500) with a pronounced shoulder at 465 mμ.

Anal. Calcd. for $C_{28}H_{19}N_3O_5$: C, 70.4; H, 4.0; N, 8.8. Found: C, 70.4; H, 4.5; N, 8.9.

Diphenyltriketone *sym*-benzoyl-*p*-nitrophenylhydrazone (123 mg., m.p. 206–208°) was prepared from 153 mg. of the nitroazotribenzoyl compound IX by heating at 140° for 1.5 hr. and crystallization from benzene. Crystallization from methanol raised the m.p. to 210.5–211.5°. The ultraviolet spectrum in dioxane showed λ_{max} 267 mμ (ϵ 30,200) with end absorption into the visible.

Anal. Calcd. for $C_{28}H_{19}N_3O_5$: C, 70.4; H, 4.0; N, 8.8. Found: C, 70.0; H, 4.1; N, 8.8.

Chromatography of 100 mg. of this substance in 75 ml. of benzene on 10 g. of alumina was carried out by allowing the substance to remain on the column for 0.5 hr. to promote the base-catalyzed cleavage[35] and then eluting with 600 ml. of 1:9 absolute ethanol–benzene to give after evaporation and crystallization of the residue from benzene–hexane 23 mg. (45%) of N-(*p*-nitrophenyl)-benzamide, m.p. 201–202° (lit.[36] 199°). A m.p. with an authentic sample showed no depression.

2,4,6-Trichlorobenzeneazotribenzoylmethane (X).—The coupling reaction was carried out as before with 3.0 g. (9.15 mmoles) of tribenzoylmethane and 1.18 g. (6.0 mmoles) of the diazonium chloride from 2,4,6-trichloroaniline, 2.0 ml. of 20% hydrochloric acid, 0.435 g. (6.3 mmoles) of sodium nitrite in 1.8 ml. of water followed by 7.8 g. of sodium acetate in 20 ml. of cold water. From the preparation of its potassium salt was recovered 1.8 g. of tribenzoylmethane. The coupling product, obtained after 5 min. as a sticky orange solid, was removed by filtration and recrystallized from ether (25–0°) to give 850 mg. (43% yield based on unrecovered triketone) of trichloroazotriketone X as orange-yellow crystals purified for analysis by further recrystallization from ether. The substance softened at approximately 100° and turned bright red. The infrared spectrum in methylene chloride had medium to strong absorption at 1677 (sh. at 1700) and 1601 cm.$^{-1}$. The ultraviolet-visible spectrum had λ_{max} 252 mμ (ϵ 26,800) and 443 mμ (ϵ 507).

Anal. Calcd. for $C_{28}H_{17}N_2O_3Cl_3$: C, 62.8; H, 3.2; N, 5.2. Found: C, 62.5; H, 3.5; N, 5.0.

α-2,4,6-Trichlorobenzeneazo-β-benzoyloxybenzalacetophenone.—The trichloroazotribenzoylmethane X (305 mg.) in 1 ml. of dioxane was heated at 65° for 1 hr. Evaporation of the solvent below 30° and chromatography of the residue over 30 g. of Florisil packed in hexane using methylene chloride–hexane (40:60) gave after removal of the solvent and recrystallization of the residue twice from acetone (25–0°) 70 mg. of bright red crystals, m.p. 145° when put into the bath at that temperature. The infrared spectrum in methylene chloride showed bands at 1753, 1714, 1680, 1620 and 1604 cm.$^{-1}$. The ultraviolet-visible spectrum in dioxane had λ_{max} 244 mμ (ϵ 35,300), 335 mμ (ϵ 17,400) and 467 mμ (ϵ 827).

Anal. Calcd. for $C_{28}H_{17}N_2Cl_3O_3$: C, 62.8; H, 3.2; N, 5.2. Found: C, 62.3; H, 3.5; N, 5.1.

Diphenyltriketone *sym*-Benzoyl-2,4,6-trichlorophenylhydrazone.—Evaporation of the solvent from a solution of 308 mg. of trichloroazotriketone X in 2 ml. of dioxane which had been heated at 99° for 8 hr. gave 311 mg. of hydrazone, m.p. 182–186°; crystallization from methanol gave 243 mg. of yellowish crystals, m.p. 188–189°.

The ultraviolet spectrum in dioxane had λ_{max} 267 mμ (ϵ 29,500). There was no absorption in the visible region above 430 mμ.

Anal. Calcd. for $C_{28}H_{17}Cl_3N_2O_3$: C, 62.8; H, 3.2; N, 5.2. Found: C, 62.6; H, 3.2; N, 5.1.

Cleavage of 82.5 mg. (0.15 mmole) of the hydrazone by treatment at 25–30° for 2.5 hr. with 80 mg. of zinc dust, 2.3 ml. of 95% ethanol and 0.35 ml. of 30% ammonium hydroxide gave, after filtration, evaporation of the filtrate and trituration with 4 ml. of 3 *N* hydrochloric acid, a solid which was washed with acid and water and crystallized from benzene–hexane yielding 23 mg. (51%) of N-(2,4,6-trichlorophenyl)-benzamide, m.p. 175–176° (lit.[37] m.p. 174°). There was no m.p. depression when mixed with a sample prepared from benzoyl chloride and trichloroaniline in pyridine.

Rates of Rearrangement of Benzeneazotribenzoylmethanes (I).—Dioxane was purified by treatment with boiling dilute hydrochloric acid for 12 hr. under nitrogen and then with potassium hydroxide and sodium metal.[38] It was freshly distilled from sodium before use. In all cases "dioxane: water($100 - x$:x)" designates a mixture prepared by

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(35) D. Y. Curtin and C. S. Russell, *J. Am. Chem. Soc.*, **78**, 5450 (1951).

(36) H. Hübner, *Ann.*, **208**, 292 (1881).

(37) F. D. Chattaway, K. J. P. Orton and W. H. Hurtley, *Ber.*, **32**, 3637 (1899).

(38) L. F. Fieser, "Laboratory Experiments in Organic Chemistry," Third Edition, D. C. Heath and Co., Boston, Mass., 1955, p. 285.

TABLE IV

REARRANGEMENT OF BENZENEAZOTRIBENZOYLMETHANE (I) IN DIOXANE AT 58.81 ± 0.02°

Time, min.	A_{510}	10^3[I], *M*	$10^5(k_1 \pm k_2)$, sec.$^{-1}$	A_{470}	10^3[II], *M*	[II]/ [I]$_\sigma$ [II]
0	0.315	0.945	....	0.106	0.000	...
25	.300	.900	3.26	.110	.017	0.378
80	.267	.802	3.42	.133	.078	.545
170	.227	.681	3.22	.150	.132	.500
320	.165	.495	3.37	.190	.241	.536
635	.089	.267	3.32	...	...	...
1414	.019[a]	.057	3.31	.269	.468	.527
		Av.	3.31 ± 0.01		Av. f_e	.527

[a] Corrected as described in the text.

TABLE V

REARRANGEMENT OF THE BENZENEAZOTRIBENZOYLMETHANES I, VIII, IX AND X IN DIOXANE AT 58.80 ± 0.02°

Substituent	10^3 × init. concn., moles/l.	λ_1[a] (ϵ), mμ	λ_2[b] (ϵ), mμ		$10^5(k_1 + k_2)$	f_e
H	0.945	510 (16,680)	470 (101)[c]		3.31 ± 0.01	0.527
	2.658		(541)[d]		3.47 ± .03	.474
	2.724				3.41 ± .04	.499
				Av.	3.40 ± 0.006	0.493 ± 0.022
CH_3O	2.325	530 (14,050)	470 (115)[c]		1.50 ± 0.04	0.347
	2.186		(1045)[d]		1.48 ± .06	.367
NO_2	1.351	510 (20,890)	520 (89.1)[c]		71.7 ± .9	.598
	3.921		(423)[d]		65.7 ± .8	.586
Cl_3	1.474	500 (9,230)	500 (149)[c] (655)[d]		90.0 ± .8	.825

[a] Wave length (and ϵ) used for the determination of the concentration of the starting material after coupling with R salt. [b] Wave length (and ϵ) used for determination of the concentration of the enol benzoate. [c] Value of ϵ of the benzeneazotribenzoylmethane. [d] Value of ϵ of the enol benzoate.

dilution of *x* ml. of water to a total volume of 100 ml. with dioxane. All glass equipment employed for kinetic measurements was soaked in chromic acid–sulfuric acid, rinsed with dilute ammonium hydroxide solution, demineralized water, and acetone and dried at 125°. It was stored in a desiccator over Drierite prior to use. All volumetric equipment was calibrated.

To 100.0 ml. of dioxane which had been allowed to come to the reaction temperature was added a weighed amount of azotriketone I (about 100 mg.) after which the flask was shaken and quickly returned to the bath. Aliquots were removed after about 15 min. with a 10-ml. pipet and the reaction quenched by rapid cooling to 0°. Control experiments showed that the loss of solvent was negligible (0.5%). Analyses were carried out by adding a carefully measured aliquot (about 1.0 ml.) of the quenched reaction mixture to about 20 ml. of dioxane in a 50-ml. volumetric flask. An aqueous solution of disodium 2-naphthol-3,6-disulfonate (R salt) (20 ml. of a 1.45×10^{-3} *M* solution) was added and then dioxane to bring the volume to 50 ml. After 2 hr. to ensure completion of the coupling reaction the absorbance at 510 mμ was determined and the concentration of azotriketone I calculated from the relationship $[I] - A_{510}/16.68 \times 10^3$. The denominator, ϵ, of the coupling product was the average of several standard experiments. This method gave the concentration of azotriketone I to about 1% when it was applied to standard solutions of I containing also the enol benzoate II and hydrazone III. The latter two compounds were shown not to react with R salt. Measurements near the end of a reaction, where the concentration of I was low compared to the concentrations of the products, were corrected (primarily for the absorption of the enol benzoate II) by subtracting 1/50 of the absorbance at 510 mμ of the aliquot before the final dilution and coupling reaction; this correction was made whenever it amounted to more than 2% of the absorbance at 510 mμ. The concentration of enol benzoate was determined from the absorbance at 470 mμ of the aliquot (before the final dilution and coupling) by using the following equation; ϵ_I and ϵ_{II} were found to be 101.1 and 541, respectively, and [I] was

$$A_{470} = \epsilon_I[I] + \epsilon_{II}[II]$$

determined from the coupling reaction above. Sample data are presented in Table IV.

The accumulated data with the rate constants and probable errors determined by the method of least squares are presented in Table V. Table I contains the summarized results. Rearrangements of the substituted benzeneazotribenzoylmethanes VIII, IX and X were carried out similarly with the results presented in Table V.

Rates of Rearrangement of the α-Benzeneazo-β-benzoyloxybenzalacetophenones.—Dioxane (about 50 ml.) was placed in a 50-ml. volumetric flask and allowed to come to temperature in a constant temperature bath. A weighed amount (about 30 mg.) of enol benzoate II or its substituted derivative was added to the flask which was shaken and quickly returned to the bath after being equipped with a self-sealing rubber cap. After thermal equilibrium had been reached (about 15 min.), aliquots were withdrawn with a hypodermic syringe and rapidly cooled. Blank runs showed the solvent loss to be negligible. The optical absorbance of the aliquot was determined at a wave length where the enol benzoate but not the hydrazone absorbed. The results are reported in Table VI. As a check on the method, the concentration of enol benzoate and hydrazone, determined spectrophotometrically, were added at each time in one reaction and the sum found to be constant throughout the run. In order to establish that the product in rearrangement of the enol benzoate II in dioxane–water (80–20) (Table VI) is the hydrazone III and not tribenzoylmethane, 790 mg. of azotriketone I in 5 ml. of dioxane was heated at 100° for 30 min. (7 half-lives for the disappearance of I) at which time there should be a nearly 50–50 mixture of enol benzoate II and hydrazone III. Since the half-time for the conversion of II to III is 13 hr. at 97° this process should be insignificant in 30 min. To the red solution resulting from the first rearrangement was added 1.25 ml. of water and the refluxing was continued for 75 hr. (about 6 half-times for the conversion of II to III). Evaporation under reduced pressure gave a crude solid whose infrared spectrum was that of the pure hydrazone III and showed no absorption at 1195–1200 cm.$^{-1}$ where tribenzoylmethane absorbs strongly. Crystallization from benzene gave 549 mg. (70%) of hydrazone III, m.p. 199–201°, and a second crop of 52 mg., m.p. 196–199°, was also obtained. When 408 mg. of the azotriketone I was heated for 30 min. with 20 ml. of dioxane and 5 ml. of water at 98° and the solution cooled and filtered, there was obtained 195 mg. (63%) of tribenzoylmethane, m.p. 233–237°, characterized by the infrared spectrum. Although these experiments do not rule out a small amount of the back rearrangement of II to I, it seems clear that the major course of the reaction is direct rearrangement to III.

Kinetics of the Reaction between Benzeneazotribenzoylmethane (I) and the Coupling Agents β-Naphthol, β-Naphthylamine and R-Salt.—The purification of the reagents and preparation of the equipment was carried out as described for the previous kinetic work. Data in Table III were collected at the ambient temperature of the cell-

TABLE VI

REARRANGEMENTS OF THE ENOL BENZOATES, II AND ITS DERIVATIVES, IN DIOXANE AT 97.10 ± 0.02°

Substituent	Init. concn., moles/l	Wave length, mμ	10^5k_3, sec.$^{-1}$
None	0.0017	470	1.49 ± 0.02
	.0020	470	1.46 ± 0.02
	.0012	470	<2.3[a]
p-Methoxy	.0010	475	1.13 ± 0.004
	.00065	470	1.20 ± .01
p-Nitro	.0010	515	14.5 ± .07
	.0017	515	14.0 ± .04

[a] Reaction in dioxane-water (80:20). The calculated rate constants drifted from 2.23 to 1.73 and since it was suspected that solvent escaped in this experiment the value of 2.3 is taken as an upper limit for the rate constant.

compartment. Routine checks at the beginning and end of several experiments showed that the temperature of the solutions was controlled to better than 0.5°. Other experiments were carried out in a jacketed 5-cm. cell with water from a constant temperature bath circulating through the jacket. 1-Benzeneazo-2-naphthol, m.p. 133.5–134.5° (lit.[39] 134°), was purified by crystallization from ethanol. Its visible spectrum in dioxane showed λ_{max} 472 mμ (ε 14,300) at concentrations of 10^{-5} to 10^{-4} *M*. 1-Benzeneazo-2-naphthylamine, m.p. 100–100.5° (lit.[40] 102–104°), crystallized from acetic acid-water, had λ_{max} 448 mμ (ε 13,600) at the same concentrations as the azonaphthol. Disodium 1-benzeneazo-2-naphthol-3,6-disulfonate, bright red crystals, m.p. 310°, showed λ_{max} (ε 18,500) at the same concentrations. Reactions were followed by measuring absorbances at 472, 450 and 490 mμ for the couplings with the naphthol, naphthylamine and R salt, respectively. Rate constants were obtained from a plot of log $(A_\infty - A_0)/(A_\infty - A)$ against *t*. When the plot showed curvature the initial slope was estimated. Otherwise the slope was obtained by the method of least squares. Sample data are presented in Table VII.

TABLE VII

RATE OF REACTION OF BENZENEAZOTRIBENZOYLMETHANE WITH R SALT IN DIOXANE-WATER (86:14) AT 27.4 ± 0.05°[a]

Time, min.	*A*	10^4k, sec.$^{-1}$	Time, min.	*A*	10^4k, sec.$^{-1}$
0	0.122	17.47	12	0.583	16.23
2	.248	16.42	14	.617	16.32
4	.339	16.38	16	.648	16.25
6	.418	16.37	18	.672	16.38
8	.484	16.67	20	.694	
10	.542	16.42		.787[b]	

[a] Initial concentrations were 1×10^{-5} *M* azotriketone and 1×10^{-4} *M* R salt. [b] Experimental value measured after 10 half-times.

TABLE VIII

COUPLING OF BENZENEAZOTRIBENZOYLMETHANE AND R SALT IN DIOXANE-WATER MIXTURES

Temp., °C.	Water,[a] %	[R salt]/[I]	10^4k, sec.$^{-1}$
27.4[b]	12	10	15.00 ± 0.05
27.4[b]	12	20	14.37 ± .08
27.4[b]	14	10	16.27 ± .05
27.4[b]	14	20	18.07 ± .11
28.0[c]	15	10	16.70 ± .04
27.0[c]	50	100	52.6 ± 1.3

[a] Here x% water refers to a solution made by diluting $(100 - x)$ ml. with x ml. of water to a total volume of 100 ml. [b] ± 0.05°. [c] ±0.5°.

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(39) C. Liebermann, *Ber.*, **16**, 2860 (1883).

(40) T. A. Lawson, *ibid.*, **18**, 798 (1885).

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Metal-ion Sensitive Protecting Groups in Synthesis. The Carbo-(8-quinoloxy) Substituent and its Removal by Accelerated Hydrolysis[1]

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The use of the carbo-(8-quinoloxy) group for the protection of amino nitrogen is described together with details concerning its detachment by means of metal-ion accelerated hydrolysis.

The "blocking" groups which are in common use for the protection of functions such as amino and hydroxyl from electrophilic attack during synthesis are invariably removed by use of an acid, a base or a reducing agent.[2] The objective of the present study was the development of a blocking group which could be dislodged under essentially neutral conditions and without the use of reducing or oxidizing reagents. Obviously, such a protecting group might be uniquely useful in certain highly restrictive synthetic situations. In particular, our scheme entailed as its central feature the employment of a protecting group which is extremely susceptible to metal-ion promoted hydrolysis but relatively resistant to hydrolysis in the absence of metal ion. There exists ample indication that for suitable structures an enormous acceleration of ester or amide hydrolysis by a complexing metal ion is possible. Thus, the hydrolysis of α-amino acid esters (*e.g.*, glycine ethyl ester) proceeds rapidly in aqueous solution in the presence of amino-coördinating transition metal ions (*e.g.*, Cu^{++}) under circumstances which do not lead to appreciable hydrolysis in the absence of the metal cation.[3] In addition, it is known that 0.1 *M* Cu^{++} increases the rate of hydrolysis of glycine amide at *p*H 7.9–9.25 by a factor of at least 100.[4] It appears probable in these cases that coördination occurs between the metal cation and the α-amino group and also the nearby carbonyl group which is positioned to allow weak chelation. This complex should be relatively susceptible to nucleophilic carbonyl addi-

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(1) From the Ph.D. dissertation of R. L. D., Harvard University, (1961).

(2) For reviews of such protecting groups as applied to peptide synthesis see (a) W. Grassman and E. Wunch, *Fort. Chem. Org. Nat.*, **13**, 444 (1956), and T. Wieland and B. Heinke, *Angew. Chem.*, **69**, 362 (1957).

(3) H. Kroll, *J. Am. Chem. Soc.*, **74**, 2036 (1952).

(4) L. Meriwether and F. H. Westheimer, *ibid.*, **78**, 5119 (1956).