1,3 Acyl Migrations in Unsaturated Triad (Allyloid) Systems. Rearrangements of N-(2,4-Dinitrophenyl)benzimidoyl Benzoates[1,2]

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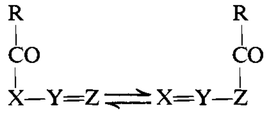
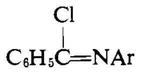
Abstract: Simple isoimides with the structure $Ar_1COOC(C_6H_5){=}NAr_2$ have been found to be sufficiently stable for isolation and study if Ar_2 contains two nitro groups (= 2,4-dinitrophenyl) to depress the nucleophilicity of the imido nitrogen atom. Thus the series of isoimides with Ar_1 = *p*-methoxyphenyl, phenyl, *p*-bromophenyl, and *p*-nitrophenyl (all with Ar_2 = 2,4-dinitrophenyl) has been prepared by the reaction of the appropriate silver benzoate with N-(2,4-dinitrophenyl)benzimidoyl chloride. These compounds rearrange to the corresponding imides (with 1,3 aroyl migration) in benzene or acetonitrile solution even at 42–65°, and kinetic measurements in this range showed that the reactions were first order and that the rates were not affected by the addition of small amounts of acetic acid or calcium hydride. The enthalpy and entropy of activation of the compound with Ar_1 = phenyl were 23.8 kcal/mole and −2.4 eu, respectively. ρ_M (measuring the effect of substituents on the migrating ring) was found to be −0.6–0.7 and the solvent dependence of the reaction expressed as an *a* value determined from comparison of the rate constant k_1 in benzene (6.1×10^{-5} sec^{-1}) with that in acetonitrile (11.8×10^{-5} sec^{-1}) of the compound with Ar_1 = phenyl was estimated to be 0.3–0.4. When the *o*-nitroimidoyl chloride, $C_6H_5CCl{=}NC_6H_4NO_2$, was treated with silver benzoate in diethyl ether, there was spectral evidence for formation of the corresponding isoimide but only the imide formed by 1,3 benzoyl migration was isolated under conditions employed for the other isoimides. It is concluded that the 4-nitro group on Ar_2 has an important effect in slowing the 1,3 acyl migration (*i.e.*, that ρ_N, the measure of effect of substituents on this ring, is negative and of appreciable magnitude). An intramolecular carbonyl addition mechanism of the type commonly considered for these and other reactions is supported by the results. Comparison of the nmr spectra of the dimethoxy compound $4\text{-}CH_3OCOOC(CH_3OC_6H_4){=}NC_6H_3(NO_2)_2\text{-}2,4$ with previously obtained imine spectra[14] provides evidence that the isoimides discussed here exist predominantly as the stereoisomer with the two aryl groups attached to the atoms of the carbon–nitrogen double bond *trans* to one another and with the likelihood that *cis–trans* interconversion at this bond is rapid compared to the measured rates of rearrangement with acyl migration. The rearrangement of N-phenylphthalisoimide to the N-phenylphthalimide[18] has been reinvestigated and the half-time for this reaction in chlorobenzene at 250° found to be about 24 hr. Reactions of this isoimide show first-order kinetics with $k_1 = 6.5 \times 10^{-5}$ in dioxane and 4.0×10^{-5} sec^{-1} in nitrobenzene at 178.23°, but it seems unlikely that these are simple internal carbonyl addition reactions. It is proposed that the 1,3 acyl migration represented by $RCOX{-}Y{=}Z \rightleftharpoons X{=}Y{-}ZCOR$ and proceeding by a four-membered cyclic transition is generally capable of occurring even at temperatures of 100° or lower and in nonpolar solvents provided both X and Z are nucleophilic atoms. On the other hand, if either X or Z is a carbon atom it is proposed on stereoelectronic grounds that such an intramolecular acyl transfer should be difficult. Therefore, the rearrangements of benzeneazotribenzoylmethane (XXV) involving 1,3 benzoyl migrations from carbon to oxygen and from carbon to nitrogen atoms have been reinvestigated. Comparison of the rates of conversion of the azo triketone XXV to the enol benzoate XXVI and benzoylhydrazone XXVII in benzene at 55.55° with the previously determined measurements in dioxane suggests that, as was previously proposed, the value of *a*, the measure of solvent sensitivity, is less than 0.1. It is further found that radical intermediates, if present in the rearrangement of XXV to XXVI and XXVII, are not intercepted by galvinoxyl or by carbon tetrachloride employed as solvent. The structurally simpler azo ketone, benzeneazobenzoyldiphenylmethane (XXX), has been prepared by the coupling of benzenediazonium fluoroborate with the sodium derivative of α-phenyldesoxybenzoin prepared from sodium hydride and the ketone in dimethyl sulfoxide. The azo compound XXX, however, did not undergo an acyl migration but instead decomposed in benzene with the loss of nitrogen to give biphenyl in a yield of 61–72%. The rate was first order and k_1 was estimated at 64.5 ± 1° to be 3×10^{-4} sec^{-1}.

As part of another investigation it was desired to have information concerning the characteristics of an intramolecular acyl migration in an unsaturated triad system shown in its most general form as the interconversion of A and B. The rearrangement of simple isoimides (or imino anhydrides) appeared attractive for study since, although such compounds had not been isolated, they had frequently been suspected as reaction intermediates. For example, imidoyl chloride I reacts with silver benzoate in ether to give not III, the product of simple nucleophilic substitution, but instead IV, the product derived from III by an acyl migration from an oxygen to a nitrogen atom.[4,5] In order to slow the



$$\underset{\textstyle A}{\overset{\overset{\textstyle R}{|}}{\underset{|}{CO}}\atop X{-}Y{=}Z} \rightleftharpoons \underset{\textstyle B}{\overset{\overset{\textstyle R}{|}}{\underset{|}{CO}}\atop X{=}Y{-}Z}$$



$$C_6H_5\overset{\overset{\textstyle Cl}{|}}{C}{=}NAr$$

I, Ar = C_6H_5
II, Ar = $2,4\text{-}(NO_2)_2C_6H_3$
VII, Ar = $2\text{-}NO_2C_6H_4$

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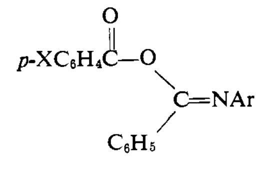
[1] Taken in part from the Ph.D. thesis of L. L. Miller, University of Illinois, 1964. Grateful acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society, for a grant providing partial support of this work.

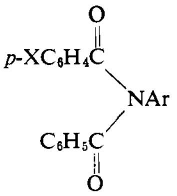
[2] For a preliminary report of this work, see D. Y. Curtin and L. L. Miller, *Tetrahedron Letters*, 1869 (1965).

[3] Eli Lilly Fellow, 1963–1964.

[4] O. Mumm, H. Hesse, and H. Volquartz, *Ber.*, **48**, 379 (1915).

[5] See J. W. Schulenberg and S. Archer, *Org. Reactions*, **14**, 1 (1965), for a review of this reaction and the (in part) closely related Chapman rearrangement.





III, Ar = C_6H_5; X = H
V, Ar = 2,4-$(NO_2)_2C_6H_3$

IV, Ar = C_6H_5; X = H
VI, Ar = 2,4-$(NO_2)_2C_6H_3$

a, X = H
b, X = CH_3O
c, X = Br
d, X = NO_2

acyl migration to permit convenient isolation of the isoimide, two nitro groups were placed on the N-phenyl ring of the imidoyl chloride I. The desired dinitroimidoyl chloride II was prepared from 2,4-dinitrobenzanilide and phosphorus pentachloride in 67% yield. It reacted readily with silver benzoate in dry ether to give a product which, when maintained below 25° during purification, was shown to be the desired isoimide Va. The structure of isoimide Va was indicated by the infrared absorption at 1750 (enol ester carbonyl) and 1680 (C=N) cm^{-1} (in benzene solution the carbonyl absorption occurred at 1763 cm^{-1}). Comparison may be made with the dimethyltriazolylisoimide[6] $(CH_3)_2C_2N_3N{=}C(C_6H_5)OCOC_6H_5$ (absorption at 1750 and 1639 cm^{-1}) and with the enol benzoate,[7] $C_6H_5N{=}NC(COC_6H_5){=}C(C_6H_5)OCOC_6H_5$ (absorption at 1745 cm^{-1}), as well as with previously reported[8] isomaleimides and isosuccinimides (with sharp absorption at about 1790 and 1700 cm^{-1}). (Allowance must be made for the five-membered ring of the latter two classes of compounds.) Support for the structural assignment of Va was provided by the extremely ready hydrolysis by concentrated hydrochloric acid (5 min at room temperature) to 2,4-dinitrobenzanilide. Absorption at 1775 cm^{-1} in the crude hydrolysis product is attributed to the presence of benzoyl chloride. The behavior of Va on melting suggested that chemical reaction was occurring on heating; the crystals melted at 90°, resolidified near 100°, and remelted at 171.5–173°, the melting point of the dibenzoylimide VIa. The dibenzoylimide VIa was prepared for comparison by treatment of 2,4-dinitroaniline with benzoyl chloride. It showed no strong absorption in the infrared spectrum (chloroform solution) between 1725 and 1800 cm^{-1} but had carbonyl absorption in benzene solution at 1715 cm^{-1}. Treatment with concentrated hydrochloric acid solution under the conditions employed for the hydrolysis of isoimide Va gave 96% recovery of dibenzoylimide VIa. The imide VIa was hydrolyzed with ethanolic potassium hydroxide, however, to a mixture of 2,4-dinitroaniline and 2,4-dinitrobenzanilide. Similar procedures gave *p*-methoxy (Vb), *p*-bromo (Vc), and *p*-nitro (Vd) derivatives of the isoimide V which on heating rearranged like the parent compound to the corresponding dibenzoylimides VIb–d.

Rearrangements of the isoimides V in benzene or acetonitrile solution to the imides VI at temperatures between 42 and 65° were followed using infrared spectroscopy to measure the rate of appearance of the maximum near 1715 cm^{-1}. First-order plots were linear to 95% reaction. The rate of rearrangement of Va was not affected by the addition of small amounts of acetic acid or calcium hydride. Rate constants were calculated with a weighted least-squares program,[9] and the average values and ranges are presented in Table I.

Table I. Rates of Rearrangement of Isoimides V to Dibenzoylimides VI

Substituent X (isoimide V)	Solvent	Temp, °C	10^5k_1, sec^{-1} (range of values)^a	ΔH^*, kcal/mole	ΔS^*, cal/mole deg
H	Benzene	42.86	6.06 ± 0.44^b		
		54.45	26.7 ± 1.2^c	23.8	−2.4
		64.44	72.3		
	Acetonitrile	42.86	11.8 ± 1.6^d		
CH_3O		42.86	5.89 ± 0.28^c		
Br		42.86	15.2 ± 3.1^c		
NO_2		42.86	33.4 ± 0.5^c		

[a] Standard deviations for individual rate constants ranged from 1 to 5.6% of the value of k with 11 of the 7 being less than 3%, and only three k's having standard deviation greater than 4%. [b] Average of five values. [c] Average of two values. [d] Average of three values.

The good first-order behavior and insensitivity of the reaction to small amounts of acid or acid scavenger suggest that the rearrangement is intramolecular. As shown by the data in Table I, the reaction is accelerated by nitro and bromo substituents on the migrating group which have a positive σ. A plot of log k against Hammett's σ constant permits a straight line to be drawn through the points belonging to the nitro, bromo, and hydrogen substituents but with the methoxyl point well below the line. ρ for substitution on the migrating group, ρ_M, calculated from the three substituents other than methoxyl is + 0.59, and the value from a least-squares treatment of all of the data is +0.69. Whatever the origin of the apparent curvature the value of about +0.6 for ρ_M may be compared with the ρ of 0.518 reported[10] for the reaction of *meta*- and *para*-substituted methyl benzoates with aniline in nitrobenzene at 80°. Although no quantitative measure was made of the effect of substituents on the N-phenyl ring (ρ_N), the repeated failures of other investigators to isolate isoimides related to Va, but without the two nitro groups on the N-phenyl rings, may be considered as evidence that ρ_N is negative and of appreciable magnitude. More pertinent is the observation made earlier[4] and confirmed during the present investigation that the 2-nitrochloroimide VII gave with silver benzoate, under conditions employed for conversion of the dinitro chloroimide II to the isoimides V, only the rearrangement product, the dibenzoylimide. Comparison with the previous studies[11] of intermolecular acylation of amides, insofar as it can be made, again indicates that the isoimide rearrangement has substituent effects qualitatively similar to those of intermolecular examples. Thus, in the reactions of *meta*- and *para*-substituted anilines with a range of acid derivatives and solvents

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[6] D. Y. Curtin and N. Alexandrou, *Tetrahedron*, **19**, 1697 (1963).

[7] D. Y. Curtin and M. L. Poutsma, *J. Am. Chem. Soc.*, **84**, 4887, 4892 (1962).

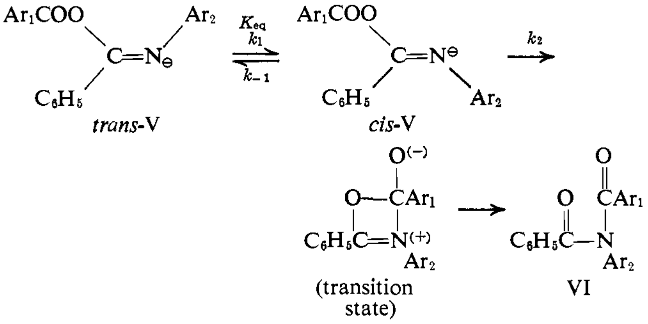
[8] (a) See E. Hedaya, R. L. Hinman, and S. Theodoropulos, *J. Org. Chem.*, **31**, 1311 (1966), for a summary and literature references; (b) E. Hedaya, R. L. Hinman, and S. Theodoropulos, *ibid.*, **31**, 1325 (1966).

[9] S. G. Smith and J. Petrovitch, unpublished work; J. Petrovitch, Ph.D. Thesis, University of Illinois, 1964.

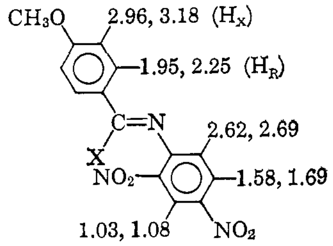
[10] N. T. Vartak, N. L. Phalnikar, and B. V. Bhide, *J. Indian Chem. Soc.*, **24**, 131A (1947).

[11] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); see particularly Table 2, Section IV, p 206 ff.

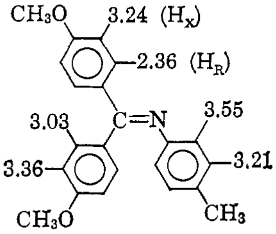
ρ was found to be -2.4 to -4. Although no detailed study of the solvent dependence of the rearrangements of the isoimides V was made, a comparison of the value of k_1 in benzene (6.1×10^{-5}) with that in acetonitrile (11.8×10^{-5}) at the same temperature gives an estimated a value[12] of between 0.3 and 0.4, large enough to suggest appreciable charge separation in the transition state. These are the characteristics of a normal carbonyl addition mechanism and lead to the following unoriginal proposal for the rearrangement mechanism. Whether there is a dipolar intermediate or merely a transition state between starting material and product cannot be answered at this point.



A more subtle question arises from the probable existence of the isoimides V in the *cis* and *trans* forms. There is no compelling evidence as to the configurations of the compounds isolated in the present work, but the destabilizing steric interaction of two *cis*-phenyl groups in related compounds such as *cis*-stilbene and *cis*-azobenzene is so great[13] as to suggest that the isomer with the two aryl groups *trans* (designated *trans*-V) is the more stable. This postulation is supported by consideration of nmr data presented here and in the Experimental Section. The most complete and unambiguous assignments of peaks were made in analysis of the spectra of the methoxyimido chloride VIII and the dimethoxyisoimide which may be compared with the dimethoxybenzophenone imine (X) previously discussed.[14] Positions of ring proton absorptions of, first, chloride VIII and, second, ester IX are shown. The most striking point for comparison is the agreement of the ring proton resonances in positions 2 and 3 of the $CH_3OC_6\mathit{H}_4C{=}N-$ unit of VIII and IX with the corresponding protons of the *trans* ring (but not the *cis*) of IX. In particular the values of $H_X - H_R$ of 1.01 and 0.93 for this ring in the chloride VIII and isoimide IX are much closer to the value of $H_X - H_R$ of 0.88 of the *trans* ring of model compound IX than to the corresponding value of 0.33 of the *cis* ring.

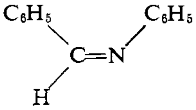


VIII, X = Cl
IX, X = p-$CH_3OC_6H_4COO$

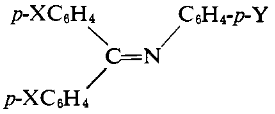


X

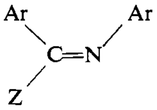
Attempts to find evidence for a second stereoisomer of Vc by irradiation of an isooctane solution for 10 min with a medium-pressure Hanovia lamp followed by immediate measurement of the ultraviolet spectrum showed only a certain amount of irreversible change. It is evident that, if the isoimide V is stored to a great extent in the *trans* form, the observed rate constant k_{obsd} cannot be a simple measure of the isomerization rate. Thus application of the steady-state approximation gives the following analysis. In the first of the two commonly considered limiting cases, that where the velocity of isomerization of *cis*- to *trans*-V is very small relative to the velocity of acyl migration (*i.e.*, $k_{-1} << k_2$), the observed rate would be simply the rate of isomerization of *trans*-V to *cis*-V (*i.e.*, $k_{obsd} = k_1$). Several lines of argument indicate that this is not the situation in the isoimide rearrangement. Although there is no direct evidence as to the rate of *cis–trans* interconversion *cis*-benzalaniline (XI) has been shown by flash-photolysis studies[15] to isomerize in ethanol or methylcyclohexane with a first-order rate of about 10 sec^{-1} (extrapolated to the temperatures employed in the present work), and triarylimines of the type XII isomerize with first-order constants again ranging about 10 sec^{-1} in nonpolar solvents at the temperatures of the present study; the rate would be expected to be even greater with nitro groups on the N-phenyl ring.[13] The inference from these earlier studies that *syn–anti* isomerization is rather insensitive to changes in substituent Z (formula C) makes it probable that the *cis–trans* isomerization of the isoimides V is considerably faster than the reaction being observed here with $k_{obsd} = 10^{-4}$–10^{-5} sec^{-1}. Additional assurance that k_{obsd} is not the rate constant for conversion of *trans*- to *cis*-V comes from consideration of the ρ value obtained which appears unreasonably large for an effect of substituents so remote from the site of isomerization.[14] The second possible limiting case is that in which *cis*-V reverts to *trans*-V much more rapidly than it undergoes acyl migration (*i.e.*, $k_{-1} >> k_2$). In this case application of the steady-state approximation shows that the observed rate constant is the product of the equilibrium constant for *cis–trans* isomerization and the rate constant for acyl migration (*i.e.*, $k_{obsd} = K_{eq}k_2$). Application of the Hammett equation to this situation gives



XI



XII



C

$$\log k_{obsd}/k_{obsd}{}^{\circ} = \sigma(\rho_{eq} + \rho_2) = \sigma\rho_{exptl}$$

Although in this case the experimental ρ is the sum of ρ_{eq} and ρ_2, it is reasonable to suppose that ρ_{eq} should be

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[12] S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961); S. G. Smith, *ibid.*, **83**, 4285 (1961).

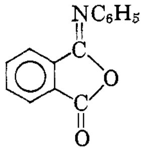
[13] See E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 342 ff.

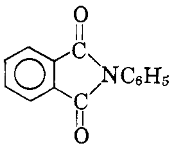
[14] D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Am. Chem. Soc.*, 88, 2775 (1966).

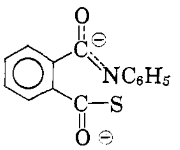
[15] E. Fischer and Y. Frei, *J. Chem. Phys.*, 27, 808 (1957); D. G. Anderson and G. Wettermark, *J. Am. Chem. Soc.*, **87**, 1433 (1965).

very small since it is a measure of the effect of change of substituents at a site remote from the carbon–nitrogen double bond; also, substituent effects have been found to be small even when the substitution was less remote as in the p-X-substituted benzophenone imines.[16] It is likely, therefore, that the experimental ρ is a valid measure of the effect of substituents on the 1,3 acyl migration although the true value of k_2 may be larger than k_{obsd} by a factor of $1/K_{\text{eq}}$. A significant result of this analysis is that the isolation of the isoimides V may well have been made possible in part because of the storage of V as the unreactive *trans* isomer. A further point is that the seeming curvature in the σ–ρ plot may be due to a change in the relative values of the k's and a partial switch from one kinetic situation to another.

It has been recognized for some time that particular stability is conferred on isoimides which are sterically constrained in such a way that the cyclic carbonyl addition mechanism through a four-membered cyclic transition state is difficult or impossible.[17] Even such compounds undergo rearrangement to the diacylimide under sufficiently severe conditions.[17] For example,

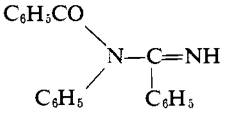

XIII

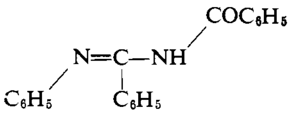

XIV


XV

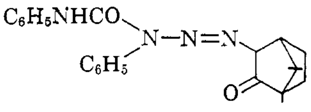
N-phenylphthalisoimide (XIII), although stable toward heating in acetic anhydride, was found to isomerize to the diacylimide XIV when the melt was heated at 250°.[18] Such rearrangements are known to be acid and base catalyzed.[17] We undertook a study of the rearrangement of isoimide XIII to the diacylimide XIV for comparison with the acyclic isoimides V. The isoimide XIII was quite stable in chlorobenzene solution at 178°, and at 250° in this solvent the half-time for rearrangement was about 24 hr. In dimethylformamide infrared analysis indicated one reaction was 90% complete only after 4 hr at 140° while a later reaction gave a 95% yield of the product XIV after 30 min at 135°. Reactions in dioxane and nitrobenzene appeared to be first order at 178.23° with $k_1 \approx 6.5 \times 10^{-5}$ and 4.0×10^{-5} sec^{-1}, respectively. No reaction occurred after a comparable length of time in chlorobenzene. It seems unlikely in view of the constraint imposed by the lactone ring that the isoimide XIII undergoes an appreciable amount of unimolecular internal acyl migration under any of the conditions employed here. Basic solvents (or impurities in them) may act as acyl group transfer agents by attack at the carbonyl group to give intermediates of the type XV.

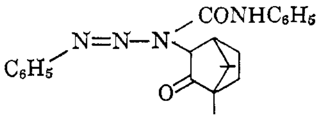
Acyl Migrations in Other Unsaturated Triad Systems. Although there seem to have been few detailed studies of such reactions, intramolecular 1,3 acyl migrations to and from reasonably nucleophilic atoms such as nitrogen and oxygen appear capable of occurring quite generally even in nonpolar solvents under relatively mild conditions. An acyl migration to and from an oxygen atom leads, of course, to a product identical with the starting material in the absence of isotopic labeling; such rearrangements have not yet been observed. Rearrangements from one nitrogen to the other of amidines have been known for many years to proceed under mild conditions even without any solvent. Thus, Wheeler, Johnson, and McFarland[19] found that the benzoylphenylbenzamidine (XVI), a crystalline solid, mp 97°, rearranges when allowed to stand for some time or on attempted recrystallization from ethanol to the isomer XVII.

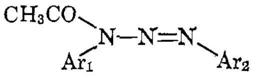

XVI


XVII

N,N acyl migration in an N-acyltriazene was first proposed by Forster and Garland[20] with the report that the acyltriazene XVIII rearranged partially on attempted recrystallization from acetone, pyridine, and alcohols and in quantitative yield in boiling pyridine to the isomer XIX. A more detailed study has been made[21] of the reactions of N-acetyldiaryltriazenes (XX) which

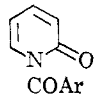

XVIII

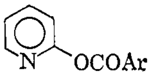

XIX


XX

undergo a first-order isomerization in benzene solution at 95° with N,N acetyl migration at a rate which is competitive with dissociation into free radicals with cleavage of the N–N single bond.

Of the rearrangements between nitrogen and oxygen in addition to the isoimide-to-diacylimide rearrangement discussed in this paper, an important family of rearrangements from nitrogen appears to have been largely overlooked. Thus, the rarity of N-acylpyridones (XXI)[22] as products of the acylation of 2-pyridone salts suggests that there may be N-acylation (at least in part) followed by a rapid rearrangement of the N- to O-acylpyridine.[23] In addition it may be noted that


XXI


XXII

N- to O-aryl (but not the alkyl) migrations (the

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[16] D. Y. Curtin and J. W. Hausser, *J. Am. Chem. Soc.*, **83**, 3574 (1961).

[17] See ref 8b and literature therein cited.

[18] M. M. Hoogewerff and W. A. van Drop, *Rec. Trav. Chim.*, **12**, 12 (1893); **13**, 96 (1895); **14**, 252 (1896).

[19] H. L. Wheeler, T. B. Johnson, and D. F. McFarland, *J. Am. Chem. Soc.*, **25**, 790 (1903).

[20] M. O. Forster and C. S. Garland, *J. Chem. Soc.*, **95**, 2051 (1909).

[21] D. Y. Curtin, J. D. Druliner, and G. Koshel, in preparation; J. D. D., Ph.D. Thesis, University of Illinois, 1966.

[22] H. Meislich, "Heterocyclic Compounds, Pyridine and Its Derivatives," Part III, E. Klingsberg, Ed., Interscience Publishers, New York, N. Y., 1962, pp 643–646.

[23] Preliminary work by Mr. J. H. Engelmann in these laboratories has supported this hypothesis. The sodium salt of 2-pyridone suspended in benzene reacts with aroyl chlorides to give rise both to the carbonyl absorption attributed to the pyridyl ester XXII (at 1730–1760 cm^{-1}) and to a second carbonyl absorption between 1675 and 1685 cm^{-1}, believed to be due to the N-acylated compound XXI, which disappears when the solution stands at room temperature. This work is being continued.

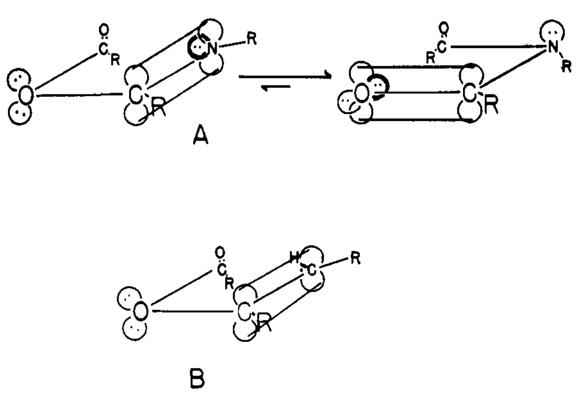


Figure 1. (A) Stereochemistry of the isoimide–imide rearrangement. (B) Enol ester stereochemistry.

Chapman rearrangement)[5,24] appear to be closely related to the acyl migrations. A rearrangement with acyl migration from nitrogen to oxygen occurs as one step of the much-investigated N-nitrosoamide decomposition.[25] This survey is summarized in Table II.

Table II. Survey of Some 1,3 Acyl Migrations

$$\begin{array}{c} \mathrm{RCO} \\ | \\ \mathrm{X{-}Y{=}Z} \end{array} \rightleftarrows \begin{array}{c} \mathrm{RCO} \\ | \\ \mathrm{X{=}Y{-}Z} \end{array}$$

X	Z	Y	Example	Ref
Oxygen	Oxygen	Carbon or nitrogen	Not yet known	
Nitrogen	Nitrogen	Carbon	N-Acylamidines	19
Nitrogen	Nitrogen	Nitrogen	N-Acyltriazenes	20, 21
Nitrogen	Oxygen	Carbon	Isoimides–diacylimides	This work, 22
Nitrogen	Oxygen	Nitrogen	N-Nitrosoamides	24

Reactions of the kinds discussed above, in order to occur uncatalyzed in nonpolar solvents at low temperatures, have certain requirements which may be considered here. In addition to the requirement that a four-membered cyclic transition state be formed without excessive strain due to distortion of bond angles, there is a more subtle stereoelectronic requirement which is illustrated in Figure 1 for the isoimide-to-diacylimide rearrangement; to achieve an optimum path from starting material to product it is necessary that there be a σ orbital with an unshared electron pair on the atom to which the acyl group is migrating. By microscopic reversibility there must be a corresponding orbital on the atom in the product to which the acyl group would migrate in the reverse rearrangement. It is evident that if the acyl migration is to occur either from or to a carbon atom, the optimum stereoelectronic requirements are not provided.[26]

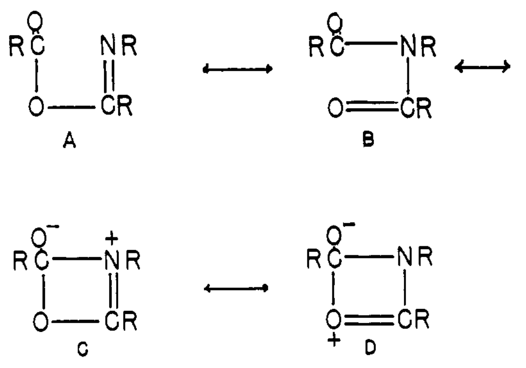
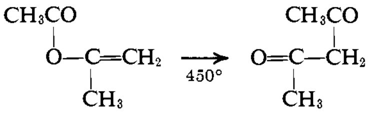


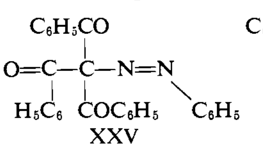
Figure 2. Transition state for concerted O- to N-acyl migration.

For example, in Figure 1B, it will be seen that a smooth development of a σ bond between the acyl carbon atom and an olefinic carbon atom requires the introduction of considerable extra strain due to the necessity of rotation of the olefinic carbon atom to permit gradual overlap between a p orbital initially perpendicular to the plane of the ring and a p orbital of the carbonyl carbon atom initially in the plane of the ring. A second disadvantage may be introduced if migration must occur to or from a carbon atom; any stabilization acquired in an N-to-N, an O-to-O, or an N-to-O (or O-to-N) rearrangement by having bond-making lead bond-breaking with the development of a transition state with charge separation is seriously reduced since resonance structures corresponding to C or D of Figure 2 are not possible contributors.



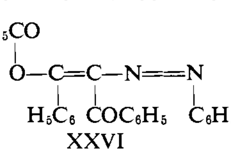
$$\mathrm{CH_3CO{-}O{-}C(CH_3){=}CH_2 \xrightarrow[450^\circ]{} O{=}C(CH_3){-}CH_2{-}COCH_3}$$

XXIII XXIV



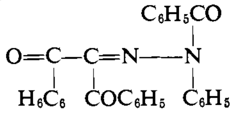
$$\mathrm{O{=}C(H_5C_6){-}C(C_6H_5CO)(COC_6H_5){-}N{=}N{-}C_6H_5}$$

XXV



$$\mathrm{C_6H_5CO{-}O{-}C(H_5C_6){=}C(COC_6H_5){-}N{=}N{-}C_6H_5}$$

XXVI



$$\mathrm{O{=}C(H_5C_6){-}C(COC_6H_5){=}N{-}N(C_6H_5CO)(C_6H_5)}$$

XXVII

Although the thermal rearrangement of enol esters to β-diketones such as the conversion of XXIII to XXIV has long been known,[27] it is not surprising in the light of the preceding discussion that such rearrangements occur only at temperatures above 200°, and commonly above 400°, and studies of the reaction have led to the conclusion[25] that it proceeds by a free-radical (dissociative) path rather than by a molecular (internal carbonyl addition) mechanism. The rearrangements to XXVI and XXVII (C-to-O and C-to-N) undergone by benzeneazotribenzoylmethane (XXV) and related compounds in nonpolar solvents[7] and in the solid state[28] are formally similar to the other reactions discussed here, but their reaction mechanisms are not yet settled. There are a number of points of difference between these reactions and the isoimide rearrangement which is the principal subject of the present paper. Thus, the effects of substituents both on the migrating benzoyl group (ρ_M) and on the aromatic ring attached to the nitrogen atom

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[24] K. B. Wiberg, T. M. Shryne, and R. R. Kintner, *J. Am. Chem. Soc.*, **79**, 3160 (1957).

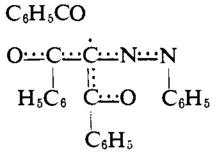
[25] For previous references, see D. B. Denney, N. E. Gershman, and A. Appelbaum, *ibid.*, **86**, 3180 (1964); E. L. Eliel and J. G. Saha, *ibid.*, **86**, 3581 (1964); C. Ruchardt and B. Freudenberg, *Tetrahedron Letters*, 3625 (1964).

[26] An alternative view of the stereoelectronic difficulty with the migration from a carbon atom has been presented previously.[7]

[27] See H. G. Hauthal, *Tetrahedron Letters*, 759 (1966), for a recent detailed study of this reaction and references to earlier work.

[28] R. T. Puckett, C. E. Pfluger, and D. Y. Curtin, *J. Am. Chem. Soc.*, **88**, 4637 (1966).

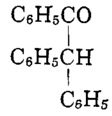
to which rearrangement is proceeding (ρ_N) seem to be opposite in the two types of rearrangement. The solvent effect in the isoimide rearrangement is considerably larger (a = 0.3–0.4) than in the rearrangements of XXV to XXVI and XXVII.[29] In view of the possibility of a mechanism involving intermediate radicals XXVIII, the rearrangement of the azo compound XXV was carried out in degassed benzene solution in the presence of an equimolar amount of galvinoxyl as a radical trap.[30]



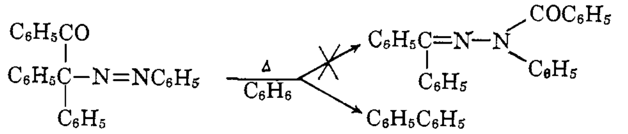
XXVIII

Less than 1% of the galvinoxyl was attacked as shown by observation of its characteristic absorption at 770 mμ, and the products XXVI and XXVII were formed in their usual high yield. Since benzoyl radicals are known[31] to attack carbon tetrachloride to form benzoyl chloride, the rearrangement of the azotribenzoylmethane (XXV) was carried out in the solvent (degassed) but with the formation of no detectable benzoyl chloride under conditions which would have permitted the detection of 1%.[32] It can only be concluded that the mechanisms of acyl migrations from carbon to oxygen and nitrogen in the azo triketones XXV remain unsettled, but there is ample reason to doubt that they are simple acyl migrations *via* a four-membered carbonyl addition mechanism analogous to the isoimide rearrangements presented in this paper.[33]

In a search for a simpler model for study of these acyl migrations from carbon to nitrogen it was of interest to prepare the analog of azo triketone XXV in which two of the benzoyl groups were replaced by phenyl rings, benzeneazobenzoyldiphenylmethane (XXX). This substance was prepared from α-phenyldesoxybenzoin (XXIX) by conversion to the sodium salt by treatment with sodium hydride in dimethyl sulfoxide followed by coupling with benzenediazonium fluoroborate. When heated in benzene, however, it did not undergo rearrangement with acyl migration but instead decomposed with the loss of nitrogen to give a 70% yield of biphenyl. The rate of disappearance of the azo ketone XXX, treated as a first-order reaction, was followed spectrophotometrically at 64.5 ± 1°, and a k_1 of about 3 × 10^{-4} was obtained. Since the total rate of acyl migration of the tribenzoyl compound XXV at 53° is 2 × 10^{-4} sec^{-1}, the failure to observe acyl migration in the reaction of the diphenyl compound XXX is due probably to a combination of accelerated free-radical decomposition to give $C_6H_5CO(C_6H_5)_2C\cdot$ as well as a decrease to an unknown extent in the rate of acyl migration. It is of interest to note that replacement of the benzoyl group of XXX by a hydrogen atom gives a molecule (benzeneazodiphenylmethane) which has been found[34] to decompose at 54° with k_1 = 1.0 × 10^{-4}, while the substance benzeneazotriphenylmethane,[35] derived from XXX by replacement of the benzoyl group by phenyl, decomposes at 53° in toluene with k_1 = 2.25 × 10^{-4} sec^{-1}.



XXIX



XXX

Experimental Section

All melting points are corrected. Some of the infrared spectra were obtained by Mr. D. Johnson and his associates with a Perkin-Elmer Model 21 or 521 spectrophotometer. Nmr spectra were provided by Mr. D. Johnson and his associates with a Varian Model

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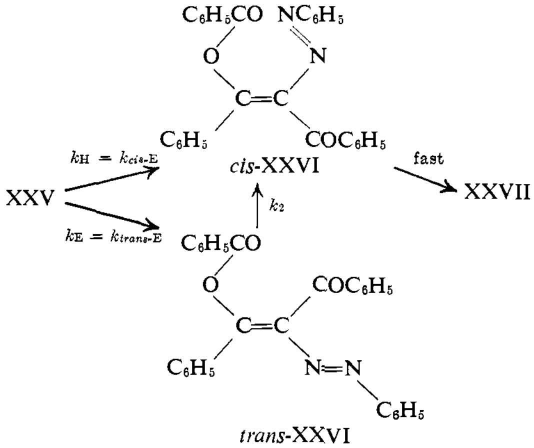
[29] The previous estimate[7] was $a < 0.1$. We have measured the rate of rearrangement of XXII in benzene at 55.55° and found it to be 2.30 × 10^{-5} sec^{-1}. Extrapolation of the previously measured[7] rate of disappearance of XXII in dioxane at 58.50 to 55.55° gives a value of 2.35 × 10^{-6} sec^{-1}. Reasonable estimates based on these data suggest that the upper limit of a is not larger than that previously given. The value of f_E (the fraction of enol benzoate XXVI) formed in benzene was 0.48 compared with 0.49 found previously[7] in dioxane.

[30] G. Coppinger, *J. Am. Chem. Soc.*, 79, 501 (1957).

[31] S. Winstein and F. H. Seubold, Jr., *ibid.*, 69, 2916 (1947).

[32] Very preliminary results have shown that the benzeneazo triketone XXV heated in *p*-xylene for 15 min at 100° and then quenched in liquid nitrogen and the frozen solution examined in an esr spectrometer gave a broad resonance without adequately resolved fine structure. No esr signal was obtained when dioxane was employed as the solvent or when xylene was employed without XXV. It has not been established further whether any radicals which may have been formed bear any relationship to the rearrangement. We are indebted to Professor H. S. Gutowsky and Dr. R. A. Meinzer for facilities and assistance with the esr measurements.

[33] An alternative interpretation of the rearrangements of azo triketone XXV to enol benzoate XXVI and hydrazone XXVII has been considered. Suppose that there is no direct rearrangement from XXV to the hydrazone XXVII with acyl migration from carbon to nitrogen but, instead, XXV undergoes competing migrations to *cis*- and *trans*-enol benzoate XXVI. If it is further assumed that the *trans*-XXVI is stable under the reaction conditions but that the *cis* isomer undergoes a very rapid further rearrangement to the hydrazone XXVII (possibly by a cyclic mechanism), the significance of the previously measured rate constants[7] is transformed as follows. The original k_E becomes $k_{trans\text{-}E}$ while k_H becomes $k_{cis\text{-}E}$. The rate constant k_2 for the slower inversion of the enol benzoate to hydrazone is then the rate constant for conversion of *trans*-enol benzoate to the *cis* isomer.



trans-XXVI

The most striking weakness of this interpretation is its premise that acyl migration to oxygen with the formation of relatively unstable products takes precedence over rearrangement to nitrogen (ordinarily a more nucleophilic atom) with the formation of a considerably more stable product. However, it cannot be rigorously excluded with the available data and, in any case, a detailed knowledge of these rearrangements demands information about the stereochemistry of the enol benzoates XXVI. The structure of a *p*-bromo derivative of XXVI is currently under X-ray crystallographic investigation by Dr. I. C. Paul and J. C. McCullough, Jr.

[34] S. G. Cohen and H. C. Wang, *J. Am. Chem. Soc.*, 77, 3628 (1955).

[35] S. G. Cohen and H. C. Wang, *ibid.*, 75, 5504 (1953).

A-60 spectrometer. Ultraviolet-visible spectra were obtained with a Bausch and Lomb Model 505 or Cary Model 14M spectrophotometer. Microanalyses were performed by Mr. J. Nemeth and his associates.

N-(2,4-Dinitrophenyl)benzimidoyl Chloride (II). 2,4-Dinitrobenzanilide[36] (28.7 g, 0.10 mole) was heated under reflux for 2 hr with 21.4 g (0.10 mole) of PCl_5 in 50 ml of benzene. After removal of volatile residue with a rotary evaporator the remaining slushy mixture was filtered and washed with hexane. Recrystallization from benzene gave 20.4 g (67%) of II, mp 117.5–120.5°. The nmr spectrum (DCl_3) showed absorption attributed to the 3-proton (doublet, τ 1.01, J = 3 cps), the 4-proton (quartet, τ 1.53, J = 3, J' = 9 cps), and the 6-proton (doublet, τ 2.79, J' = 9 cps) of the dinitrophenyl ring plus complex absorption attributed to the protons of the phenyl ring.

When 2.0 g of the chloride II was warmed for 15 min with 15 ml of water in 15 ml of dioxane and a small amount of sodium carbonate, there was formed a yellow oil which solidified on cooling and, after washing with water and recrystallization from xylene, was found to be 1.0 g (60%) of 2,4-dinitrobenzanilide, mp 200–202.5°, by a comparison of its infrared spectrum with that of an authentic sample. When 1.0 g of chloride II was treated with 1 equiv of potassium hydroxide in ethanol, there was obtained 300 mg (60%) of dinitroaniline as shown by comparison of infrared spectrum and melting point and mixture melting point with an authentic sample.

Anal. Calcd for $C_{13}H_8N_3O_4Cl$: C, 51.1; H, 2.6; N, 13.8; Cl, 11.6. Found: C, 51.2; H, 2.7; N, 13.7; Cl, 11.3.

N-(2,4-Dinitrophenyl)benzimidoyl Benzoate (Va). The chloride II (9.5 g, 35 mmoles) was stirred for 16 hr with 7.5 g (33 mmoles) of dry silver benzoate prepared from silver nitrate and sodium benzoate in 70 ml of ether. The resulting suspension was filtered and the precipitate washed with ether. Evaporation of the ether from the filtrate gave 6.1 g of pale orange Va which after five recrystallizations from toluene-hexane (solution at room temperature diluted with hexane and cooled to 0° to induce crystallization) gave 300 mg (3%) of Va as nearly white crystals, mp 90° (resolidifying at about 100° and remelting at 171.5–173°). The preparation of Va could also be carried out by treating silver benzoate with chloride II in acetone or dimethyl sulfoxide but with, apparently, more side reaction to yield a red oil, not identified, than the procedure above. Sodium benzoate and II in ether gave only unreacted II after 30 hr in ether at room temperature.

The infrared spectrum of Va (KBr disk) showed important bands at 1750, 1680, 1530, and 1340 cm^{-1}. The 1750-cm^{-1} band appeared at 1763 cm^{-1} in benzene solution with ϵ 650. The nmr spectrum of the dinitrophenyl ring resembled that of the corresponding ring in the chloroimide II with absorption attributed to the 3-, 4- and 6-protons centered at τ 1.15, 1.68, and 2.80 (?), respectively. In addition there was complex absorption centered at τ 1.9 and 2.4 due to the other ring protons.

Isoimide Va (100 mg, 0.26 mmole) suspended in 2 ml of concentrated hydrochloric acid for 5 min gave, after neutralization with 10% sodium bicarbonate, 70 mg (96%) of solid with an infrared spectrum almost identical with that of 2,4-dinitrobenzanilide except for a band at 1775 cm^{-1} attributed to benzoyl chloride. Thin layer chromatography on silica gel G (eluted with methylene chloride and developed with potassium permanganate spray) showed only a single spot with the same R_f as an authentic sample. Separation of the spot and trituration with ethanol gave a solution with λ_{max} 303 mμ and between 260 and 230 mμ (ratio of absorbances at 303 and 250 mμ was 1.1).

N-(2,4-Dinitrophenyl)dibenzoylimide (VIa). Addition of 67 ml (0.4 mole) of benzoyl chloride to 24 g (0.13 mole) of 2,4-dinitroaniline suspended in 65 ml of aniline and heating for 4.5 hr at 90° gave, after cooling and addition to 450 ml of 2 *N* hydrochloric acid, 48 g of a mixture of benzoyl derivatives which when recrystallized three times from ethanol had mp 158–165°, unchanged by a further recrystallization. Exhaustive sublimation at 0.5-mm pressure gave 2,4-dinitrobenzanilide, mp 196–199°, as the sublimate and the dibenzoylimide VIa as the residue, mp 173.5–174.5°. The infrared spectrum (chloroform) showed absorption at 1685, 1655 (sh), 1525, and 1330 cm^{-1}. The ultraviolet spectrum (ethanol) had λ_{max} 245 (ϵ 26,400) with a shoulder at 285 mμ. The nmr spectrum (deuteriochloroform) showed absorption characteristic of the 3- and 5-protons of the dinitrophenyl ring as in the compounds above at τ 1.07 (area 1.0, J = 4 cps) and 1.69 (area, 0.9, J = 4,9 cps) together with complex multiplets at τ 2.25 (area 6.8) and 2.63 (area 4.2).

Treatment of 108 mg of the imide VIa, 170.5–173.5°, with 0.2 ml of concentrated hydrochloric acid followed by neutralization after 5 min with aqueous sodium bicarbonate gave 103 mg of starting material, mp 171–175°, with the infrared spectrum unchanged. When a solution of 394 mg of VIa and 150 mg of potassium hydroxide in 10 ml of ethanol was warmed to the boiling point, cooled to room temperature, neutralized with hydrochloric acid, and filtered, there was obtained a precipitate of 135 mg (47%) of 2,4-dinitrobenzanilide, mp 198–201° (infrared spectrum superimposable on that of an authentic sample). Evaporation of the ethanol from the filtrate gave 50 mg (27%) of 2,4-dinitroaniline, mp 176–178°, as shown by the infrared spectrum and comparison of the R_f value obtained by thin layer chromatography on silica G, eluting with ethyl acetate.

N-(2,4-Dinitrophenyl)benzimidoyl 4-methoxybenzoate (Vb) was prepared from 25 g of imino chloride II and 35 g of dry silver anisate in ether by the method employed for Va. Extraction of the solid product with chloroform and evaporation of the chloroform gave solid Vb, mp 142–143.5°, after recrystallization from chloroform by adding hexane at room temperature and cooling to 0°. A first fraction was identified as anisic acid, mp 182.5–185° (lit.[37] mp 184°). The isoimide had strong infrared absorption (KBr disk) at 1740, 1675, 1610, 1525, 1515, and 1348 cm^{-1}.

Anal. Calcd for $C_{21}H_{15}N_3O_7$: C, 59.9; H, 3.6; N, 10.0. Found: C, 59.7; H, 3.6; N, 9.9.

N-(2,4-Dinitrophenyl)benzoyl-4-methoxybenzoylimide (VIb). The isoimide Vb was heated to 120°, where it melted and resolidified to give after fractional crystallization from acetone 0.8 g (73%) of VIb, mp 165–173°, together with a first fraction of 0.2 g of 2,4-dinitrobenzanilide, mp 196–199°, identified by its infrared spectrum. Recrystallization of VIb from ethanol gave mp 171.5–173°. The infrared spectrum (KBr disk) had absorption at 1700, 1670, 1605, 1540, 1515, and 1350 cm^{-1}.

Anal. Calcd for $C_{21}H_{15}N_3O_7$: C, 59.9; H, 3.6; N, 10.0. Found: C, 59.8; H, 3.6; N, 9.8.

N-(2,4-Dinitrophenyl)benzimidoyl 4-Bromobenzoate (Vc). The reaction of silver *p*-bromobenzoate with the chloroimide II and purification of the product, carried out as with the *p*-methoxy compound Vb, gave isoimide mp 128–132°, with partial resolidification at higher temperatures. The infrared spectrum (KBr disk) showed absorption at 1750, 1685, 1610, 1535, and 1345 cm^{-1}.

Anal. Calcd for $C_{21}H_{15}N_3O_7Br$: C, 51.1; H, 2.6; Br, 17.0; N, 8.9. Found: C, 51.2; H, 2.6; Br, 16.9; N, 8.8.

N-(2,4-Dinitrophenyl)benzoyl-4-bromobenzoylimide (VIc). The isoimide Vc was heated to a melt and allowed to resolidify. Crystallization from ethanol and then benzene gave imide VIc, mp 156–160°. The infrared spectrum showed the presence of an amide impurity (absorption at 3400 cm^{-1}), so the product was further purified by sublimation at 0.5-mm pressure to give yellow 2,4-dinitrobenzanilide, mp 191–198°, and the imide VIc, mp 166–167°. The infrared spectrum (KBr disk) showed absorption at 1710, 1695, 1610, 1590, 1540, and 1350 cm^{-1} with a shoulder at 1330 cm^{-1}.

Anal. Calcd for $C_{20}H_{12}BrN_3O_6$: C, 51.1; H, 2.6; Br, 17.0; N, 8.9. Found: C, 51.2; H, 2.7; Br, 17.2; N, 8.8.

N-(2,4-Dinitrophenyl)benzimidoyl 4-nitrobenzoate (Vd) was prepared and isolated (24% yield) by the procedure employed for the other substituted isoimides V. When heated it softened at 135°, resolidified, and melted at 198–199.5°. The infrared spectrum (KBr disk) showed absorption at 1755, 1690, 1610, 1530, and 1340 cm^{-1}.

Anal. Calcd for $C_{20}H_{12}N_4O_8$: C, 55.1; H, 2.8; N, 12.8. Found: C, 54.7; H, 2.6; N, 12.6.

N-(2,4-Dinitrophenyl)benzoyl-4-nitrobenzoylimide (VId), mp 197–199°, after recrystallization from ethanol, was prepared in 80% yield by heating isoimide Vd to a melt and cooling. Further recrystallization from ethyl acetate gave mp 198–199.5°. The infrared spectrum (KBr disk) had absorption at 1710, 1680, 1610, 1535, and 1350 cm^{-1}.

Anal. Calcd for $C_{20}H_{12}N_4O_8$: C, 55.1; H, 2.8; N, 12.8. Found: C, 55.1; H, 2.9; N, 12.7.

Reaction of N-(2-Nitrobenzimidoyl) Chloride (VII) with Silver Benzoate. Repetition of the reaction of the imidoyl chloride VII with silver benzoate, previously reported[4] and carried out by the procedure described above for other isoimides, gave an ether solution which showed absorption at 1740 cm^{-1}, but isolation gave a

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(36) M. F. Muttelet, *Bull Soc. Chim. France*, [3] 19, 519 (1898).

(37) T. R. Lea and R. Robinson, *J. Chem. Soc.*, 2355 (1926).

52% yield of the rearrangement product, N-(2-nitrophenyl)dibenzoylimide, mp 179–182° (lit.[4] 182°), shown by its infrared spectrum (KBr disk) to have strong absorption at 1710 cm^{-1} but with no absorption at 1740–50 cm^{-1}, in agreement with the earlier structural assignment.[4]

N-(2,4-Dinitrophenyl)-4-methoxybenzimidoyl Chloride (VIII). Reaction of 32 g (0.1 mole) of 4-methoxy-2,4-dinitrobenzanilide, mp 185–188° (from anisoyl chloride and 2,4-dinitroaniline), with 21 g of PCl_5 in 50 ml of benzene gave, after 2 hr under reflux and evaporation of volatile material, 31 g (93%) of imidoyl chloride VIII, mp 109–116°. Recrystallization from benzene gave mp 113–117°.

Anal. Calcd for $C_{14}H_{10}ClN_3O_5$: C, 50.1; H, 3.0; Cl, 10.6; N, 12.5. Found: C, 50.1; H, 3.1; Cl, 10.4; N, 12.3.

N-(2,4-Dinitrophenyl)-4-methoxybenzimidoyl 4-Methoxybenzoate (IX). Reaction of 16 g of the chloride VIII with 12 g of silver anisate as in the synthesis of other isoimides in 200 ml of dry ether which had been cooled to 0° was allowed to proceed for 15 min at 0° and then warmed to room temperature over a period of 3 hr. After filtration of some anisic acid, the residue was washed with 200 ml of ether and then extracted with benzene which on evaporation left 7 g of 4-methoxy-2,4-dinitrobenzanilide (removed by filtration) and finally 500 mg of pale yellow solid IX, mp 102–105°. The infrared spectrum showed absorption at 1730 and 1660 cm^{-1}. The product was quite unstable. On standing for 2 weeks the melting point had risen to 105–112°. Further recrystallization gave a yellow solid, mp 185–187°, presumed to be 4-methoxy-2,4-dinitrobenzanilide, and a material, mp 140–145°, not identified.

Anal. Calcd for $C_{22}H_{17}N_3O_8$: C, 58.5; H, 3.8; N, 9.3. Found: C, 57.8; H, 3.7; N, 9.5.

N-(2,4-Dinitrophenyl)di(4-methoxybenzoyl)imide (IX). When the reaction of 23 g (0.07 mole) of the imidoyl chloride VIII was allowed to react with silver anisoate in 200 ml of dry ether without prior cooling, the reaction mixture became warm and after 6 hr of work-up by the method employed for the isoimides V gave first 0.7 g of anisic acid, mp 176–178° (confirmed by infrared spectrum), then 4.0 g of 4-methoxy-2,4-dinitrobenzanilide, and finally a yellow glass which crystallized when warmed in ether and had mp 155–158°. Further recrystallization gave a material with mp 158–160° which resolidified on cooling and remelted at the same temperature. Its infrared spectrum (Nujol mull) had bands at 1690, 1650, 1600, 1570, 1530, and 1340 cm^{-1}. The nmr spectrum (deuteriochloroform) showed methoxyl absorption (singlet) at τ 6.13, H_X absorption of the methoxy-substituted ring at τ 3.01 (doublet), H_R absorption at τ 1.96, 3-H absorption of the dinitro-substituted aromatic ring at τ 1.05, 5-H absorption at τ 1.60, and 6-H absorption at τ 2.58 (relative areas, 5.9, 3.7, 4.1, 1.2, 1.0, and 1.1.)

Anal. Calcd for $C_{22}H_{17}N_3O_8$: C, 58.5; H, 3.8; N, 9.3. Found: C, 58.8; H, 4.3; N, 9.5.

Rates of Rearrangement of the N-Dinitrophenylbenzimidoyl Benzoates V. Benzene was purified by distillation from Drierite. Acetonitrile was distilled from P_2O_5, dried over K_2CO_3, and distilled again over P_2O_5. Sample tubes were cleaned by soaking in potassium dichromate–sulfuric acid followed by rinsing with dilute aqueous ammonia and distilled ammonia or simply by soaking in deionized water. In either case they were then rinsed with acetone and dried in an oven. A 0.3-ml aliquot of a standard solution of the isoimide V was placed in each tube to be employed for a kinetic run and the tube cooled in Dry Ice-acetone and sealed. The bath temperature was controlled to ±0.04° and its temperature measured with a Beckmann thermometer checked against a thermometer calibrated by the National Bureau of Standards. The rate of disappearance of the isoimide carbonyl band (1763 cm^{-1}) was followed when Va was examined in benzene containing acetic acid. In all other cases the appearance of the absorption due to the rearrangement product VI was followed. In each case Beer's law plots determined with standard solutions were shown to be linear in the concentration range being employed. The rate constants were calculated by an IBM 7094 computer with a least-squares program[9] which calculated the slope of a plot of ln Y *vs.* time where

$$Y = \frac{A_\infty - A_0}{A_\infty - A}$$

and values of Y were weighted by the factor $|Y - Y_\infty|$. The computer program also rejected points with a deviation of Y from the line amounting to greater than three times the standard deviation. An iterative method led to the selection of ln Y_∞ which minimized the standard deviation in the slope. Infinity absorbances in kinetic runs were within 5% of the value calculated from the original concentration of isoimide. In one case the solution from a kinetic run in benzene was evaporated, and the solid had mp 169–170°. Spectra agree with those of the dibenzoylimide. Sample data are presented in Table III. Detailed data are available in the thesis of Miller.[1]

Table III. Rearrangement of 0.029 *M* Isoimide Va in Benzene at 42.86 ± 0.04°[a]

Time, min	*A*	Weight	10^4k, sec^{-1}
0	0.041	0.173	0.6104
1,800	0.059	0.155	0.6201
4,485	0.083	0.131	0.7259
8,850	0.123	0.091	0.6404
13,260	0.140	0.074	0.5927
18,150	0.155	0.059	0.6227
24,340	0.176	0.038	0.7572
35,240	0.202	0.000	
46,700	0.212		
90,000	0.216		

A (infinity) = 0.214

k = 0.622 x 10^{-4} sec^{-1}

Std dev = 0.023 x 10^{-4}

[a] Employing the absorbance at 1714 cm^{-1} and a 0.1-mm cell.

Rearrangement of N-Phenylphthalisoimide (XIII). The isoimide XIII, mp 114–115° (from acetone) (lit. 116°[18], 112°[35]), was best prepared by dehydrating N-phenylphthalamic acid with acetyl chloride[18] followed by extraction with carbon disulfide and the suspension in ether and extraction with aqueous sodium bicarbonate. Results using the trifluoride-acetic anhydride procedure[38] were erratic. The infrared spectrum (KBr disk) showed absorption at 1775, 1700, 930, and 720 cm^{-1}. The ultraviolet spectrum (ether solution) had λ_{max} 327 (ϵ 9500) and 297 mμ (ϵ 7100) with an inflection at 245 mμ. Chlorobenzene was purified by shaking with successive portions of concentrated sulfuric acid until the acid layer was no longer colored, then with water, dilute sodium bicarbonate, and water, and finally dried and distilled.[39] The absorbance at 918 cm^{-1} due to the isoimide XIII changed from 0.55 to 0.49 after heating at 178° for 16 hr. At 212° there was no change in 3 hr, but after 12 hr the absorbance had decreased from 0.55 to 0.52. A solution 0.115 *M* in XIII held at 254° was about one-half reacted after 23 hr (as estimated from the decrease in absorption at 930 cm^{-1}) and after 48 hr the infrared spectrum was superimposable on that of the rearrangement product XIV.[18] Addition of benzoyl peroxide or azobisisobutyrylnitrile had no dramatic effect on the rearrangement of XIII in chlorobenzene.

In dimethylformamide purified by the method of Smith, Fainberg, and Winstein,[12] a 94% yield of the imide XIV, mp 206–210°, was obtained after 30 min at 135°. However, the rate was not reproduced from one reaction to another, and the infrared spectrum of one solution changed even at room temperature after several hours. Details of reactions in dioxane and nitrobenzene are available in the thesis of Miller.[1]

Rearrangement of Benzeneazotribenzoylmethane (XXV) in Benzene. Rate and Effect of Galvinoxyl. The method employed for measurement of the rates was that reported[7] previously. Benzene was purified by distillation from Drierite and dioxane by the method of Fieser.[40] The rate constants for disappearance of XXV and probable errors (obtained by the method of least squares with no weighting of points) together with the fraction of enol benzoate (f_E) formed were for a reaction at 55.50 ± 0.05°: $k_1 = 2.31 \pm 0.02 \times 10^{-5}$ sec^{-1}, $f_E^{av} = 0.499 \pm 0.014$; and at 55.60 ± 0.05°: $k_1 = 2.28 \pm 0.02 \times 10^{-5}$ sec^{-1}, $f_E^{av} = 0.463 \pm 0.013$.

When 237 mg (0.55 mmole) of azo triketone XXV and 123 mg (0.29 mmole) of purified galvinoxyl in 10 ml of benzene were degassed (0.5 mm) and sealed in a combustion tube and then heated at 55.6° for 44 hr and 90° for 76 hr, there was obtained on removal of the solvent 175 mg (74%) of hydrazone XXVII, mp 197–200°, mmp

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(38) W. R. Roderick and P. L. Bhatia, *J. Org. Chem.*, 28, 2018 (1963).

(39) K. B. Wiberg, "Laboratory Techniques in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 240 ff.

(40) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1955, p 284.

(mixed with an authentic sample) 199.5–201°. In other reactions for times of 1077 and 510 min, solutions of azo compound (0.0012 and 0.011 *M*) were heated with galvinoxyl (0.0009 and 0.0015 *M*). The tubes were compared with blanks containing only azo compound and controls containing only galvinoxyl. The disappearance of galvinoxyl was followed in the near-infrared spectrum by the change in absorbance at 770 mμ. After correction from the absorbances of the standard solutions the per cent trapping was calculated as follows.

$$\%\ \text{trapping} = \text{(change in galvinoxyl concentration)}/2 \times \text{change in azo concentration}$$

The per cent trapping was found to be 0.8 and 0.04. Another similar run for 111 min gave a value of 1.0%.

Reaction of Azo Triketone XXV in Carbon Tetrachloride. When 18 mg (0.042 mmole) of azo triketone XXV in 10 ml of carbon tetrachloride, degassed at 0.5 mm in a sealed tube, was heated for 30 hr at 65°, there was obtained a bright red solution with no detectable absorption at 1775 cm^{-1} (due to benzoyl chloride) leading to an upper limit of 0.3% of this product. A control experiment with 0.012 mmole of benzoyl chloride in 0.27 mmole of hydrazone XXVII showed that removal of the solvent led to isolation of 87% of the hydrazone and in the filtrate was undecomposed benzoyl chloride as shown by absorption at 1775 and 1745 cm^{-1}. In another experiment 177 mg of azo triketone XXV and 10 μl of benzoyl chloride in 100 ml of reagent grade carbon tetrachloride were heated for 15 hr at 65° after which the spectrum showed absorption at 1775 cm^{-1}. Concentration of the solution gave 132 mg (74%) of hydrazone XXV, mp 198–199°, and the filtrate had absorbance 0.33 of the 1775-cm^{-1} band, indicating almost complete survival of the benzoyl chloride.

Benzeneazodiphenylbenzoylmethane (XXV). Phenyldesoxybenzoin (XXIX), 2.72 g, 10 mmoles, mp 136–137°, in 80 ml of dimethyl sulfoxide (purified by passing through a column of Type 4a Molecular Sieves) was treated in a nitrogen atmosphere with 0.46 g (10 mmoles) of a 52% sodium hydride dispersion in mineral oil. To the resulting bright red solution was added 1.91 g (10 mmoles) of benzenediazonium fluoroborate. After 20 min 200 ml of ice water was added. Extraction with ether and concentration of the ether solution gave 1.95 g (54%) of azo compound as yellow crystals which were purified by solution in acetone, addition of water to the cloud point, and cooling for 10 hr. The product XXX, shiny yellow needles, decomposed on heating, but at a heating rate of 1°/min the decomposition point was 113°. With β-naphthylamine there was formed a red solution presumed to be indicative of coupling. The ultraviolet spectrum of XXX in chloroform showed λ_{max} 415 (ϵ 290). The infrared spectrum (chloroform) had absorption at 1680, 1600, 1490, and 1445 cm^{-1}.

Anal. Calcd for $C_{26}H_{20}N_2O$: C, 83.0; H, 5.3; N, 7.5. Found: C, 83.0; H, 5.5; N, 7.7.

Decomposition of Azo Compound XXX in Benzene. When 2.97 g (7.9 mmoles) of XXX was heated in 40 ml of benzene at 65° for 6 hr (visible gas evolution for the first 2 hr) and the benzene distilled, there was obtained a yellow oil. Addition of cyclohexane gave 400 mg (13%) of product whose infrared and ultraviolet spectra were very similar to those of phenyldesoxybenzoin (XXIX). Chromatography of the remaining product on silica gel (elution with 30% benzene in hexane) gave a hydrocarbon fraction (169 mg) which was estimated by ultraviolet analysis to contain a 71% yield of biphenyl, and by vapor phase chromatography on an 8 ft Qf-1 column at 179° (flow rate 60 ml/min) to contain 62% of biphenyl. The rate of decomposition of XXX in benzene (64.5 ± 1°) was determined by heating a solution in a volumetric flask and withdrawing aliquots at times from 4 to 780 min; a plot (five points) of $\ln (A_0 - A_\infty)/(A - A_\infty)$ *vs.* time gave a reasonable straight line with a *k* determined from the slope of 2.6×10^{-4}.

Photosensitized Rearrangements of Triarylmethyl Azides[1]

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Abstract: The loss of nitrogen and rearrangement to benzophenone phenylimine of triphenylmethyl azide can be effected by photolysis in the presence of a variety of triplet sensitizers. The sensitizers definitely produced a reaction range in triplet energy from 67.6 kcal/mole (fluorene) to 48.7 kcal/mole (pyrene), so the triplet energy of triphenylmethyl azide must be less than 48.7 kcal/mole. Migration aptitudes in the photolysis sensitized by triphenylene of diphenyl(*p*-X-phenyl)methyl azides (X = NO_2, Cl, CH_3, OCH_3, $N(CH_3)_2$) were all close to unity, as previously observed[3] in the direct photolysis. It is concluded that both the direct and sensitized photolyses involve a triplet azide and probably a discrete triplet nitrene as intermediates.

In earlier work on azides we observed that the migration aptitude of *para*-substituted phenyl relative to phenyl depended on the electronic character of the substituent in the thermal,[2] but not in the photochemical,[3] rearrangement. We suggested that the thermal rearrangement was a concerted process with some degree of aryl participation, but that the photochemical process involved a discrete nitrene intermediate. While a triplet appeared more likely than a singlet nitrene as the intermediate, no firm conclusion could be reached. Consequently, we decided to examine the role of triplet intermediates by determining whether the reaction could be effected by triplet sensitizers.

Photosensitized reactions of a number of organic azides have been reported,[4-6] and esr signals attributable to triplet nitrenes have been observed in photolyses of organic azides in glasses[7] and single crystals.[8] Previous workers used benzophenone[5,6] or acetophenone[4] as sensitizers, but we found that photolysis products from the sensitizers greatly complicated the work-up of our reaction mixtures when these substances were

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