1,3 Acyl Migrations in the Thermal Decomposition of N-Acyltriazenes[1]

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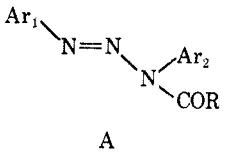
A synthesis of N-acyldiaryltriazenes by coupling of an arenediazonium fluoroborate with the sodium salt of an amide prepared from sodium hydride and the amide in tetrahydrofuran has been found. Not only is this method convenient but it gives unsymmetrical N-acyltriazenes in a way that resolves the structural ambiguity associated with synthesis by acylation of the preformed triazene. Prepared by this method were N-acetyldiphenyltriazene (H/H-I), N- and N′-acetyl-N-(*p*-methoxyphenyl)-N′-(*p*-chlorophenyl)triazene, (Cl/CH_3O-I and CH_3O/Cl-I), N- and N′-acetyl-N-(*p*-methoxyphenyl)-N′-(*p*-trifluoromethylphenyl)triazene (CF_3/CH_3O-I and CH_3O/CF_3-I), and N-acetyl-N-(*p*-nitrophenyl)-N′-(*p*-methoxyphenyl)triazene (CH_3O/NO_2-I). These compounds have been found, in agreement with reports of other investigators, to undergo thermal decomposition by a homolytic mechanism. Additional evidence for the mechanism has been provided by a study of the decomposition of H/H-I in nitrobenzene which gives *o*-, *m*-, and *p*-biphenyl in relative amounts of 65:7:28 in good agreement with the isomer ratio previously reported[11] for phenylation of nitrobenzene with benzoyl peroxide. The decompositions of the unsymmetrical N-acetyltriazenes (X/Y-I) were found to be complicated by a 1,3 N-N acetyl migration which occurred at a rate as great as or greater than that of the homolytic decomposition. A method employing ultraviolet spectroscopy made possible a quantitative study of the change with time of the concentrations of each of a pair of isomeric acyltriazenes during reaction in benzene at 95.00 ± 0.05° (decay of the concentration of the starting material and the accumulation and subsequent disappearance of the isomer formed by acyl migration). Plots of these data could be reproduced with an analog computer with the assumption that the reaction system was of the type $P_a \xleftarrow[k_a]{} A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow[k_b]{} P_b$ with all reactions being first order. Reactions were studied starting with both A (alone) and B (alone) and curves for each reaction were matched by the computer plots with an identical set of rate constants for the two reactions. The rate constants so obtained were as follows. The name of the compound is followed by the value of k_1, k_{-1}, k_a, and k_b, all $\times 10^4$ in units of reciprocal seconds (A has been chosen to be the isomer $XC_6H_4N{=}NN(COCH_3)C_6H_4OCH_3$ of an unsymmetrically substituted pair): H/H-I, . . . , . . . , 0.13, 0.13; CH_3O/Cl-I and Cl/CH_3O-I, 1.70, 1.71, 1.10, and 0.53; CH_3O/CF_3-I and CF_3/CH_3O-I, 1.71, 1.92, 1.90, 0.29; CH_3O/H-I and H/CH_3O-I 1.67, 1.67, 0.78, and 0.88. An attempt to prepare N-benzeneazophthalimide by a modification of the coupling method employed for the other acyltriazenes studied here was unsuccessful.

Although N-acyltriazenes (A) have known for many years[2] their chemistry has been relatively little investigated. Even the structures of many of them are in some doubt since they have been made commonly by acylation of the parent triazene, a reaction which provides no reliable indication of the position at which the acyl group is introduced. A further complication has been suggested by a report by Forster and Garland[3] that the triazene B rearranged to C with N,N acyl migration when it was heated in pyridine. The evidence for structures B and C was marginal (nitrogen analyses but no carbon and hydrogen analyses were reported for these compounds) but the relatively ready 1,3 acyl migration suggested by this work was of interest in view of other such rearrangements to and from oxygen and nitrogen atoms which have been found to occur uncatalyzed in nonpolar, even hydrocarbon, solvents under mild conditions.[4]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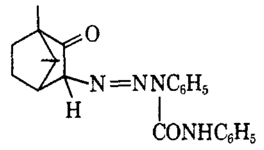
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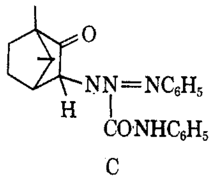
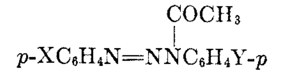
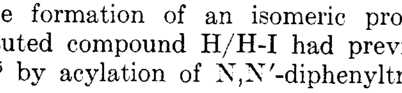

C


$$\overset{\displaystyle COCH_3}{\overset{|}{p\text{-}XC_6H_4N{=}NNC_6H_4Y\text{-}p}}$$
X/Y-I

H/H-I, X = Y = H
CH_3O/H-I, X = CH_3O; Y = H
CH_3O/Cl-I, X = CH_3O; Y = Cl
CH_3O/CF_3-I, X = CH_3O; Y = CF_3
CH_3O/NO_2-I, X = CH_3O; Y = NO_2
H/CH_3O-I, X = H; Y = CH_3O
Cl/CH_3O-I, X = Cl; Y = CH_3O
CF_3/CH_3O-I, X = CF_3; Y = CH_3O


$$XC_6H_4N{\equiv}N^+ + {}^-\overset{\displaystyle COCH_3}{\overset{|}{N}}C_6H_4\text{-}Y \longrightarrow X/Y\text{-}I$$

The compounds chosen for study were N-acetyldiphenyltriazene and certain of its unsymmetrically substituted derivatives (I). Since it was desired to prepare the unsymmetrical isomers by a method which produced a single isomer of known structure, the coupling of a diazonium salt with the sodium salt of the appropriate amide was investigated. The desired sodium salt was readily prepared by treatment of the amide with sodium hydride in tetrahydrofuran and the diazonium fluoroborate was added to the resulting solution. The product was precipitated by addition of water and recrystallized from ether or pentane. With this procedure each synthesis produced a single acyltriazene in a yield of 40–90% and there was no detectable formation of an isomeric product. The unsubstituted compound H/H-I had previously been prepared[5] by acylation of N,N′-diphenyltriazene and

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(1) Taken from the Ph.D. Thesis of J. D. Druliner, University of Illinois, 1966. Grateful acknowledgment is made to the U. S. Army Research Office (Durham) for partial support of this work.

(2) T. W. Campbell and B. F. Day, *Chem. Rev.*, **48**, 299 (1951).

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

(4) D. Y. Curtin and L. L. Miller, *J. Am. Chem. Soc.*, **89**, 637 (1967).

(5) F. Heusler, *Ber.*, **24**, 4157 (1891); P. Grammaticakis, *Compt. Rend.*, **245**, 1252 (1957).

TABLE I

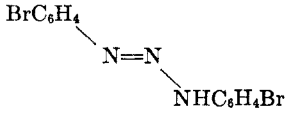
AROMATIC PROTON POSITIONS RELATIVE TO THE CORRESPONDING PROTONS IN THE SUBSTITUTED TOLUENES IN DEUTERIOCHLOROFORM SOLUTION WITH TETRAMETHYLSILANE AS AN INTERNAL STANDARD[a]

	τ, ppm, for H_X, where X is the following				τ, ppm, for H_R, where X is the following			
	CH_3O	Cl	CF_3	NO_2	CH_3O	Cl	CF_3	NO_2
$XC_6\mathit{H}_4{-}CH_3$	3.20[b]	2.90[c]	2.52[b]	1.87[c]	2.95[b]	2.98[c]	2.75[b]	2.62[c]
$XC_6\mathit{H}_4NHCOCH_3$[d]	−0.02[d]	−0.19[e]	−0.10	−0.06[f]	−0.35	−0.56[e]	−0.57	−0.51[f]
$XC_6\mathit{H}_4NN{=}NAr$[d] $\vert$ $COCH_3$	−0.20[g]	−0.39	−0.27	−0.21	+0.05[g]	+0.04	−0.03	+0.04
$XC_6\mathit{H}_4N{=}NNAr$[d] $\vert$ $COCH_3$	−0.12	−0.28	−0.15	−0.21	−0.44	−0.44	−0.38	...
$XC_6\mathit{H}_4N{=}NC_6H_5$[d] (*trans*)	−0.22	...	...	...	−0.89	...	...	...

[a] Chemical shifts were calculated with the approximation that $1 - 3 = [(\delta_A - \delta_B)^2 - J_{AB}^2]^{1/2}$ (see L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, pp 89, 90). [b] Varian Spectra Catalog, Varian Associates, Palo Alto, Calif., 1962, Spectra 157 and 205. [c] H. Rottendorf and S. Sternhell, *Tetrahedron Letters*, 1289 (1963). [d] Present work. [e] In perdeuteriodimethyl sulfoxide. [f] In perdeuterioacetone. [g] Average of values from four compounds with Ar = *p*-Cl, *p*-CF_3, *p*-NO_2, and *p*-H-phenyl.

the coupling product obtained in this work had a melting point and an ultraviolet spectrum in agreement with those previously reported.[5] CH_3O/H-I and H/CH_3O-I were first prepared by Koshel[6] using the method developed here. The physical properties found in this investigation are in agreement with those of Koshel.

Additional structural evidence may be cited. Infrared spectra of the acetyltriazenes (I) showed a strong absorption at 1700 cm^{-1} attributed to the N-acylcarbonyl group and no significant absorption above 3100 cm^{-1}. The nmr spectra, particularly those of the *para,para'*-disubstituted compounds showed aromatic A_2B_2 spectra which could be treated approximately as AB quartets or, in some cases, as singlets, and which give a reasonable pattern of chemical shift values as shown in Table I. Assignments in Table I were made in such a way as to achieve greatest internal consistency. Although the data are not of the highest possible accuracy, the reasonableness of the results serves to confirm both the assignments of nmr absorptions and the structures being considered. Thus the replacement of a methyl group in a *para*-substituted toluene by the acetamide group, $NHCOCH_3$, leads to a downfield shift of 0.46 ± 0.11 ppm of the absorption position of the protons adjacent to the methyl group (H_R), but a downfield shift of only 0.10 ± 0.09 ppm for the protons (H_X) *meta* to the methyl group. In the same way the group $N(COCH_3)N{=}NAr$ shifts the adjacent protons (H_R) only 0.00 ± 0.05 ppm and the more remote protons (H_X) downfield 0.30 ± 0.10 ppm and the grouping $N{=}NN(COCH_3)Ar$ shifts the adjacent protons (H_R) downfield 0.41 ± 0.03 and the more remote protons (H_X) downfield 0.20 ± 0.08 ppm. Although the data provide no evidence as to the configuration around the nitrogen–nitrogen double bond there was no indication of a second stereoisomer of any of these compounds and it is tentatively concluded that they are all the less sterically hindered *trans* isomers. It is relevant to this conclusion that *p,p'*-dibromodiazoaminobenzene (II, below) has been shown by X-ray crystallography to be *trans* in the solid state.[7]



$$BrC_6H_4{-}N{=}N{-}NHC_6H_4Br$$

The thermal decomposition of the parent triazenes has been studied[8] and been found to proceed by homolytic cleavage of the nitrogen–nitrogen single bond. The only study of products from the thermal decomposition of N-acyltriazenes appears to be that of Nagasaka and Oda[9] who found that unsubstituted compound H/H-I when decomposed in hot benzene solution gave biphenyl and acetanilide together with some quaterphenyl. Simple N-acyltriazenes such as H/H-I have been reported in a British patent to initiate the polymerization of styrene when heated.[10]

Initially it was desired to obtain further confirmation of the previous reports that the decomposition of N-acyltriazenes in aromatic solvents leads to a free-radical arylation reaction. The unsubstituted compound (H/H-I) was therefore decomposed in nitrobenzene at 95° and the mixture of nitrobiphenyls obtained was isolated and analyzed by gas phase chromatography. In Table II the ratio of isomeric nitrobiphenyls thus formed is compared with the results[11] of homolytic phenylation of nitrobenzene by benzoyl peroxide. It will be seen that the ratio of isomers agrees in the two reactions but is different from that obtained[11] by decomposition of benzenediazonium fluoroborate, presumably an electrophilic substitution.

TABLE II

COMPARISON OF THE RATIO OF NITROBIPHENYLS FORMED BY THE DECOMPOSITION OF N-ACETYLDIPHENYLTRIAZENE (H/H-I) IN NITROBENZENE WITH RATIOS FROM BENZOYL PEROXIDE[11] AND BENZENEDIAZONIUM FLUOROBORATE[a]

		Isomer ratio, %		
Starting material	Temp, °C	*ortho*	*meta*	*para*
H/H-I	95	65	7	28
Benzoyl peroxide[a]	80	63	10	27
Benzenediazonium fluoroborate	60	20	80	0

[a] Reference 11.

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(6) D. Y. Curtin and G. N. Koshel, in press.

(7) Y. D. Kondrashev, *Kristallografiya*, **6**, 515 (1961).

(8) See B. A. Erusalimskii, A. P. Kabuleiskii, and B. A. Dolgoplosk, *Izv. Akad. Nauk, SSSR*, 1672 (1960), and previous work cited therein; C. S. Rondestvedt, Jr., and H. S. Blanchard, *J. Am. Chem. Soc.*, **77**, 1769 (1955).

(9) A. Nagasaka and R. Oda, *Kôgyô Kagaku, Zasshi*, **59**, 571 (1956); *Chem. Abstr.*, **52**, 3742 (1958).

(10) J. Porges, J. Elly, and E. T. Burrows, British Patent 716,429 (1954); *Chem. Abstr.*, **49**, 4331 (1955).

(11) R. A. Abramovitch and J. G. Saha, *Tetrahedron*, **21**, 3297 (1965).

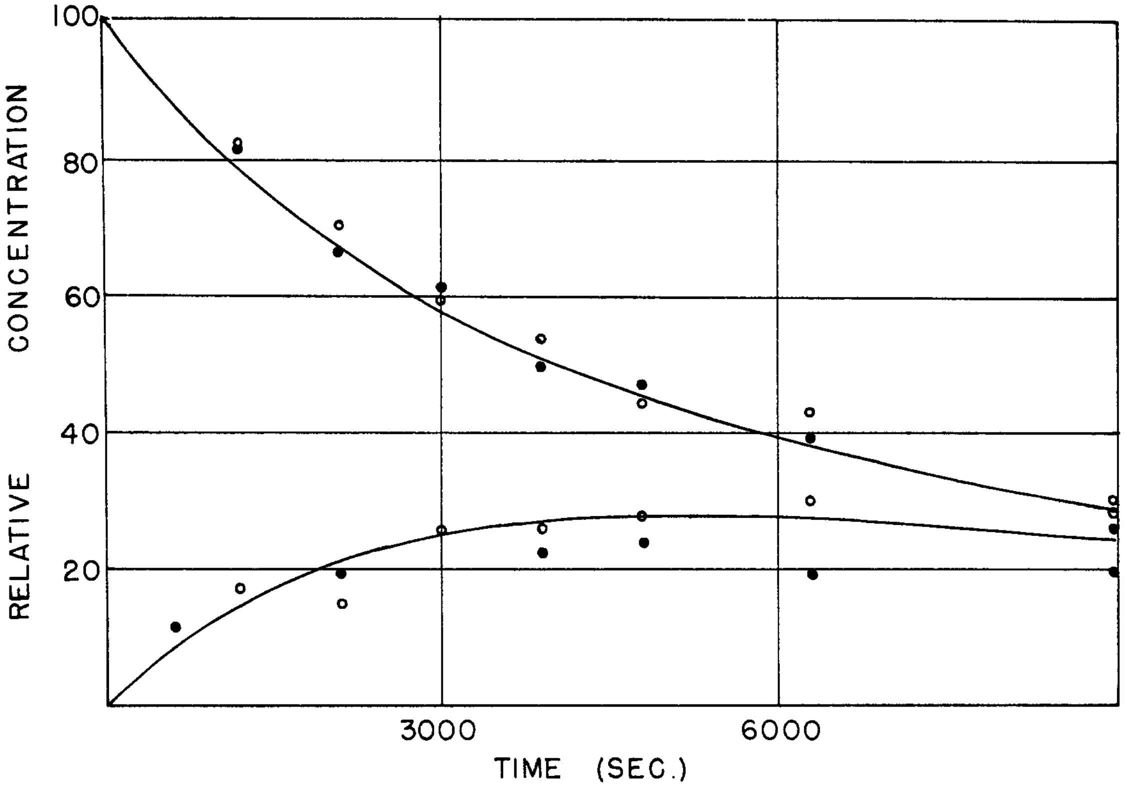
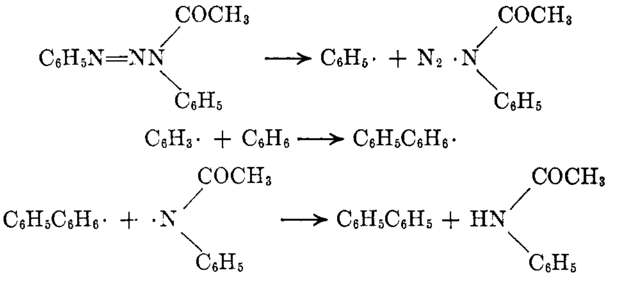


Figure 1.—Reaction of CH_3O/H-I in benzene at 95.00°. Open circles and filled circles are data from two independent reactions. The upper curve is the analog computer plot of the disappearance of CH_3O/H-I and the lower curve is the plot of the appearance and subsequent disappearance of H/CH_3O-I during the same reaction. Computer plots were obtained with values of the rate constants chosen to optimize not only the fit of these data but also data obtained with H/CH_3O-I as starting material.

The rate of decomposition of acyltriazene H/H-I in benzene at 95° followed by ultraviolet spectroscopy, was first order to past 85% reaction and the rate constant of 1.27×10^{-5} sec^{-1} did not change significantly when the concentration of starting material was varied over the range 2.26–9.87 $\times$ 10^{-2} *M*. These results are consistent with the mechanism for the major reaction path shown in Scheme I.

SCHEME I



$$C_6H_5N{=}NN(COCH_3)(C_6H_5) \longrightarrow C_6H_5\cdot + N_2 + \cdot N(COCH_3)(C_6H_5)$$

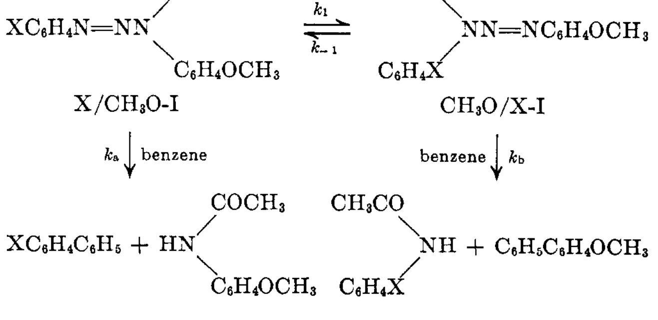
$$C_6H_5\cdot + C_6H_6 \longrightarrow C_6H_5C_6H_6\cdot$$

$$C_6H_5C_6H_6\cdot + \cdot N(COCH_3)(C_6H_5) \longrightarrow C_6H_5C_6H_5 + HN(COCH_3)(C_6H_5)$$

The acyltriazene decomposition may be subject to complications similar to those found in benzoyl peroxide decomposition[12] such as nonsynchronous breaking of the two bonds to the departing nitrogen and the possibility of induced decomposition. Since the homolytic decomposition is of interest in the present study primarily as a background against which to consider the N to N acyl migration which is now to be discussed, these complexities will be ignored here.

Because of the ease of 1,3 acyl migrations in other unsaturated triad systems[4] it appeared likely that such a rearrangement should be competitive with the homolytic decomposition of the acyltriazenes. In order for the 1,3 rearrangement to be observed, of course, the starting material must be unsymmetrically substituted and the two substituted triazenes CH_3O/Cl-I and Cl/CH_3O-I were initially chosen for study. Decomposition of Cl/CH_3O-I in benzene at 95° gave a 67% yield of a mixture of biphenyls and 97% of the theoretical amount of a mixture of acetanilides. Analysis by a combination of chromatography and ultraviolet spectroscopy showed that in addition to the *p*-chlorobiphenyl (43%) and *p*-methoxyacetanilide (41%) expected from the direct homolytic decomposition of Cl/CH_3O-I there were obtained major amounts of *p*-methoxybiphenyl (57%) and *p*-chloroacetanilide (59%), products to be expected of the decomposition of CH_3O/Cl-I, the isomer derived from the starting material by 1,3 N,N acetyl migration prior to homolysis (see Scheme II). Similarly a reaction starting with CH_3O/Cl-I was found to give both of the two possible biphenyls and both acetanilides. A direct demonstration of the rearrangement was obtained by isolation

SCHEME II



$$\underset{X/CH_3O\text{-I}}{XC_6H_4N{=}NN(COCH_3)(C_6H_4OCH_3)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{CH_3O/X\text{-I}}{(CH_3CO)(C_6H_4X)NN{=}NC_6H_4OCH_3}$$

$$X/CH_3O\text{-I} \xrightarrow[k_a]{\text{benzene}} XC_6H_4C_6H_5 + HN(COCH_3)(C_6H_4OCH_3)$$

$$CH_3O/X\text{-I} \xrightarrow[k_b]{\text{benzene}} (CH_3CO)(C_6H_4X)NH + C_6H_5C_6H_4OCH_3$$

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(12) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 474 ff.

of acyltriazene Cl/CH_3O-I from a partially completed reaction which had contained only CH_3O/Cl-I initially; no isomerization could be detected after 70 hr at ambient temperature, however. It was clear that the velocities of the acyl migration and decomposition reactions were sufficiently close to one another to prevent the use of simplifying assumptions to reduce the reaction to one with a simple kinetic order. Confirmation that the reactions interconverting the acetyltriazenes Cl/CH_3O-I and CH_3O/Cl-I as well as the homolytic decompositions giving biaryls were first order in acetyltriazene was obtained by showing that the disappearance of the initial acetyltriazene as well as the buildup and later disappearance of the acyl migration product could be simulated with reasonable precision using a Pace analog computer and adjusting the rate constants k_1, k_{-1}, k_a, and k_b to get the best correspondence with the experimental data. Concentrations of the two isomeric acetyltriazenes were determined by ultraviolet spectroscopy by the method of Dewar and Urch.[13] The data are presented in Table III. A check on the validity of the method is provided by a comparison with the experimental values of the relative net amounts of reaction by paths a and b calculated by the analog computer. The ratio of path a to path b starting with Cl/CH_3O-I calculated was 63:37 and that found was 58:42. The rearrangements of the other N-acyltriazenes, CH_3O/H-I, H/CH_3O-I, CH_3O/CF_3-I, and CF_3/CH_3O-I, were studied in the same way and the kinetic results are reported in Table III. Although the precision of the data in Table III is not high, there are a number of reassuring points of self-consistency. The effect of substituents on the equilibrium constant for acyl migration (X/Y-I $\rightleftharpoons$ Y/X-I) as measured by the ratios k_1/k_{-1} is 1.0 in each case with the possible exception of the trifluoromethyl compounds with $K_{eq} = 0.89$ whose deviation from 1.0 could be significant. In every case the rate of acyl migration is as fast as or faster than the rate of homolytic decomposition; the compound CH_3O/CF_3-I undergoes acyl migration at a rate seven times as fast as the rate of homolytic decomposition. The effect of substituents on the rates of acyl migration is of interest because of its smallness. The largest effect observed (the effect on k_{-1} of replacing a *para* hydrogen atom by a trifluoromethyl group) was only a factor of 1.1. Although there is no direct measure of the effect of substituents (X) on the N-phenyl ring in the isoimide rearrangement previously studied, it has been inferred[4] that it is sufficiently large to be of synthetic importance, the reaction being retarded by a *p*-nitro group.

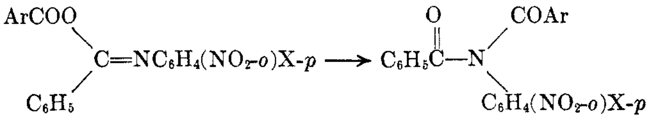
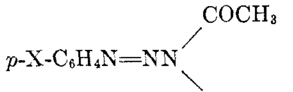


TABLE III

RATES OF 1,3 N,N ACETYL MIGRATION AND HOMOLYTIC DECOMPOSITION OF N-ACETYLTRIAZENES X/Y-I IN BENZENE AT 95.00 ± 0.05°[a]



X/Y-I

Starting material	Rate constants (10^4k, sec^{-1}) — Rearrangement k_1	(av)	k_{-1}	(av)	Homolysis k_a	(av)	k_b	(av)
CH_3O/H-I	1.67		1.67		0.63		0.92	
		1.67		1.67		0.78		0.88
H/CH_3O-I	1.67		1.67		0.92		0.84	
CH_3O/Cl-1[b]	1.53		1.83		1.19		0.56	
		1.70		1.71		1.10		0.53
Cl/CH_3O-I	1.88		1.59		1.00		0.50	
CH_3O/CF_3-I	1.75		1.83		1.83		0.33	
		1.71		1.92		1.90		0.23
CF_3/CH_3O-I	1.67		2.00		1.96		0.25	
H/H-I	...	...		...		0.13		0.13

[a] All reactions were carried out in duplicate. Both sets of data were included in points to be matched with the analog computer plots. [b] Averages of a run at 95.00 and a second carried out at 95.72 with a small correction to 95.00.

The rate constants for homolytic cleavage k_a and k_b show a somewhat greater sensitivity to changes of substituents than do the rate constants for acyl migration k_1 and k_{-1}. It is convenient to make comparisons with the assumption that effects of substituents on free energies of activation are additive.[14] The data in Table III give the following substituent effects when the rate of a disubstituted triazene X/Y-I relative to the unsubstituted compound H/H-I is separated into factors for the *p*-methoxyl group on the aromatic ring attached to the amide nitrogen atom ($f_{Am}^{OCH_3}$) or to the azo nitrogen atom ($f_{Az}^{OCH_3}$) and for the other substituents (X) in corresponding positions (f_{Az}^{X} and f_{Am}^{X}). Such substituent effects although too small to be interpreted with any assurance can be inspected for internal consistency and compared with relevant data from the literature. It will be seen that substituents on the aromatic ring attached to the amide nitrogen atom show at least a qualitative correlation with the Hammett σ constant,[14b] the methoxyl group (with a negative σ) increasing and the other two (with positive σ) decreasing the rate; the trifluoromethyl substituent having the more positive σ produces the greater rate decrease.

TABLE IV

$$k_y^x = k_H^H \times f_{Az}^x \times f_{Am}^y$$

$f_{Az}^{OCH_3}$	×6.8	$f_{Am}^{OCH_3}$	×6.0	$\sigma^{p\text{-}OCH_3}$	−0.268 (−0.778)
f_{Az}^{Cl}	×1.4	f_{Am}^{Cl}	×1/1.7	$\sigma^{p\text{-}Cl}$	+0.227
$f_{Az}^{CF_3}$	×2.4	$f_{Am}^{CF_3}$	×1/3.0	$\sigma^{p\text{-}CF_3}$	+0.54

Comparison of our data with rates of decomposition of diaryltriazenes (III) studied by Dolgoplosk, Uryumov, and Krol[15] is of interest. Although the unsubstituted compound H/H-III and the dimethyl derivative CH_3/CH_3-III failed to follow first-order kinetics, the data suggest that the acetyl group in H/H-I increases the rate of decomposition by the homolytic path by an order of magnitude. Furthermore the homolytic decomposition of III is accelerated by *p*-methyl groups and decelerated by chloro and nitro groups (the dinitro compound NO_2/NO_2-III being

$XC_3H_4N{=}NNHC_6H_4X$ $\quad$ $XC_6H_4N{=}NC(C_6H_5)_3$

X/X-III $\quad$ IV

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[13] M. J. S. Dewar and D. S. Urch, *J. Chem. Soc.*, 345 (1957).

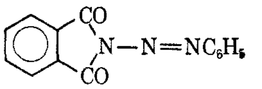
[14] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963; (a) p 155 ff; (b) p 204.

[15] B. A. Dolgoplosk, P. G. Uryumov, and V. A. Krol, *Dokl. Akad. Nauk* **96**, 757 (1954).

stable at 140°. Their substituent effects are thus qualitatively similar to those of substituents on the amide aromatic ring of our acyltriazenes (f^{X}_{Am}).

The effect of substituents in the *para* position of the phenyl ring attached to the azo nitrogen of I does not follow the Hammett relation even qualitatively. All three substituents accelerate the decomposition; again the absolute value of the effect of the trifluoromethyl substituent is greater than that of the chloro. A comparison with the effect of substituents on the decomposition of *para*-substituted benzeneazotriphenylmethanes (IV) studied by Cohen and Wang[16] shows a similar lack of correlation with the σ values of substituents. They found that *p*-bromo and *p*-nitro lowered the rate of decomposition (factors of 1/2.1 and 1/3.9, respectively) in agreement with the behavior found in the acyltriazenes, but that the *p*-methoxyl group also gave a small decrease in rate and the *p*-methyl group had no observable effect.

The coupling of benzenediazonium ion with phthalimide ion to give the diacyl triazene (V) appeared to be



V

of particular interest since it could serve as a source of the elusive phthalimidoyl free radical.[17] No coupling product was obtained when benzenediazonium fluoroborate was added to a suspension of potassium phthalimide in dimethylformamide below 0°. Instead when the potassium salt was added to the diazonium fluoroborate solution at −25° there was slow evolution of gas and development of a brown color. In another experiment the diazonium fluoroborate was shown to be stable in dimethyl formamide at −65° until the potassium phthalimide was added after which gas was again evolved. The great stability of biphthalimide makes it appear unlikely that the diacyltriazene (V), if it was ever formed, underwent a simple homolytic cleavage of the N–N bond.[17] This reaction is being investigated further.

Experimental Section

All melting points are corrected. Infrared spectra were measured with a Perkin-Elmer Model 521 spectrophotometer, nmr spectra with a Varian Model A-60 instrument, by Mr. O. Norton, Mr. D. Johnson, and their associates. Microanalyses were performed by Mr. J. Nemeth and his associates. The ultraviolet spectra were obtained with a Cary Model 14M or a Bausch and Lomb Model 505 spectrophotometer. Gas phase chromatography was carried out with an Aerograph Model A-90-P instrument. The analog computer was a Pace TR-20 instrument. Benzene was purified by distillation from molecular sieves. Spectral grade cyclohexane was checked for interfering absorption in the ultraviolet spectrum and used directly.

Absorbancy data and analog computer plots are included in the thesis of J. D. D., available from University Microfilms, Ann Arbor, Mich.

Arenediazonium fluoroborates were prepared by the addition of 25% aqueous ammonium fluoroborate to the diazotized amine; the precipitated salt, after filtration, washing with cold methanol and ether, and drying was further purified by precipitation from cold acetone (−5°; after treatment with activated charcoal) by cold ether, filtered, dried at room temperature, and stored in a vacuum desiccator. The yields and melting points were benzenediazonium fluoroborate, 82%, 93–94° (lit.[17] 100°); *p*-methoxybenzenediazonium fluoroborate, 77%, 139–139.5° (lit.[17] 142°); *p*-chlorobenzenediazonium fluoroborate, 60%, 131–132° (lit.[17] 139°); *p*-trifluoromethylbenzenediazonium fluoroborate 75%, 111–112°; *p*-nitrobenzenediazonium fluororate, 91%, 154–156° (lit.[17] 155°).

Coupling of the Diazonium Salts with Sodium Acetanilides. N-Acetyldiphenyltriazene (H/H-I).—In a typical reaction 4 mmoles of the acetanilide was converted to its sodium salt by treatment in an atmosphere of dry nitrogen with a 50:50 dispersion of sodium hydride (4 mmoles) in mineral oil in 2 ml of tetrahydrofuran which had been purified by distillation from lithium aluminum hydride. Addition of 95% of the benzenediazonium fluoroborate to the solution (cooled in an ice–salt bath) gave after addition of the reaction mixture to 200 ml of water at 5° a precipitate of the N-acyltriazene. The unsubstituted compound H/H-I after purification by recrystallization from ether was obtained as white crystals (43% yield), mp 117–119 dec (lit.[5] 129–130° dec). It was further purified by sublimation at 100° (0.5 mm) to give mp 134–135°. The ultraviolet spectrum in cyclohexane showed λ_{max} 290 mμ (ϵ 18,400) [lit.[5] λ_{max} 290 mμ (ϵ 16,000), diethyl ether]. The infrared spectrum in chloroform showed absorption at 1700 but no absorption above 3100 cm^{-1}. The nmr showed complex absorption at τ 2.35–3.00 and a singlet at 7.30 (ratio of areas 10.0:2.9).

N-Acetyl-N-(*p*-chlorophenyl)-N′-(*p*-methoxyphenyl)triazene (CH_3O/Cl-I) was prepared from *p*-chloroacetanilide[19] by the procedure above except that the product was not isolated by addition of the reaction mixture to water; instead, it could be filtered directly to give an 87% yield of product, mp 110–115°, which when purified by crystallization from ether (activated charcoal) amounted to 52% of white product mp 117° dec. The ultraviolet spectrum showed λ_{max} 316 mμ (ϵ 16,300) in cyclohexane. In addition to the aromatic spectrum (Table I) the nmr spectrum showed singlets at τ 6.2 and 7.3 (areas 8.0:2.96: 2.96).

Anal. Calcd for $C_{15}H_{14}ClN_3O_2$: C, 59.3; H, 4.6; N, 13.8. Found: C, 59.3; H, 4.6; N, 13.9.

N′-Acetyl-N-(*p*-chlorophenyl)-N′-(*p*-methoxyphenyl)triazene (Cl/CH_3O-I), prepared from *p*-methoxyacetanilide,[18] like its isomer, was obtained in a crude yield of 65% and after several recrystallizations from ether had mp 141–141.5°. The ultraviolet spectrum had λ_{max} 300 mμ (ϵ 16,900). The infrared spectrum showed strong absorption at 1700 but not above 3000 cm^{-1}. The nmr spectrum showed in addition to the aromatic spectrum (Table I) singlets at τ 6.2 and 7.3 (areas 8.2:3.1:3.1).

Anal. Calcd for $C_{15}H_{14}ClN_3O_2$: C, 59.3; H, 4.6; N, 13.8. Found: C, 59.6; H, 4.7; N, 13.8.

N-Acetyl-N-(*p*-trifluoromethylphenyl)-N′-(*p*-methoxyphenyl)-triazene (CH_3O/CF_3-I) was prepared substantially by the method used for the acyl triazenes above from *p*-methoxybenzenediazonium fluoroborate and the sodium salt of *p*-trifluoroacetanilide. In this case the formation of the sodium salt of the acetanilide required heating to 40–50° after which the coupling reaction was conducted initially at −78° and the reaction mixture was then placed in an ice–salt bath for 15 min. After filtration and washing with cold (Dry Ice–acetone) tetrahydrofuran the solvent was removed to give a 95% yield of crude product which after purification by two recrystallizations from ether–pentane had mp 100–110° dec. The ultraviolet spectrum (cyclohexane) showed λ_{max} 316 mμ (ϵ 16,300) and the infrared spectrum showed strong absorption at 1680 but none above 3100 cm^{-1}. The nmr showed, in addition to the aromatic spectrum, singlets at τ 6.17 and 7.30 (areas 8.17:2.95:2.88).

Anal. Calcd for $C_{16}H_{14}F_3N_3O_2$: C, 57.0; H, 4.2; N, 12.5. Found: C, 56.7; H, 4.0; N, 12.5.

N′-Acetyl-N-(*p*-trifluoromethylphenyl)-N′-(*p*-methoxyphenyl)-triazene (CF_3CH_3O-I) was prepared from *p*-trifluoromethylbenzenediazonium fluoroborate and *p*-methoxyacetanilide by the method employed previously for H/H-I. The crude product first obtained as an oil (99% yield) partially crystallized after storage for several hours at 0° and was purified by recrystallization to constant ultraviolet spectrum from ether and then pentane. The ultraviolet spectrum showed λ_{max} 281 (ϵ 16,500). The infrared spectrum (chloroform) had strong absorption at

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[16] S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **75**, 5504 (1953).

[17] See H. D. K. Drew and H. H. Hatt, *J. Chem. Soc.*, 16 (1937); C. Walling and A. N. Naglieri, *J. Am. Chem. Soc.*, **82**, 1820 (1960); E. Hedaya, R. L. Hinman, and S. Theodoropulos, *J. Org. Chem.*, **31**, 1317 (1966).

[18] D. Y. Curtin and J. L. Tveten, *J. Org. Chem.*, **26**, 1764 (1961).

[19] P. Grammaticakis, *Bull. Soc. Chim. France*, **220**, 534 (1951).

1700 but not above 3100 cm^{-1}. The nmr showed in addition the aromatic spectrum (Table I) singlets at τ 6.17 and 7.32 (areas 8.00:3.04:3.04).

Anal. Calcd for $C_{16}H_{14}F_3N_3O_2$: C, 57.0; H, 4.2; N, 12.5. Found: C, 56.9; H, 4.3; N, 12.6.

N-Acetyl-N-(*p*-nitrophenyl)-N′-(*p*-methoxyphenyl)triazene (CH_3O/NO_2-I) was prepared as above from *p*-methoxybenzenediazonium fluoroborate and the sodium salt of *p*-nitroacetanilide. Although the yield of crude product was 73%, extraction with 300 ml of ether gave less than 1% of product, mp 120–195°, which did not melt sharply after further purification by crystallization and chromatography. The ultraviolet spectrum (acetonitrile) showed λ_{max} at 315 mμ (ϵ 28,600). The infrared spectrum (hexachlorobutadiene Nujol mull) showed strong absorption at 1705 but no absorption above 3100 cm^{-1}. The nmr spectrum of the product recrystallized from benzene–pentane showed in addition to the aromatic proton absorption (Table I) singlets at τ 6.17 and 7.31. Attempts to prepare the isomeric compound NO_2/CH_3O-I were unsuccessful.

Anal. Calcd for $C_{15}H_{14}N_4O_4$: C, 57.3; H, 4.5; N, 17.8. Found: C, 57.4; 56.8; H, 4.9, 4.6; N, 17.5, 17.9.

Decomposition of N-Acetyldiphenyltriazene H/H-I in Nitrobenzene.—A solution of 141 mg (5.9 mmoles) of H/H-I was heated at 95.00 ± 0.05° in a sealed tube with 15.0 ml of nitrobenzene which had been purified by steam distillation and then vacuum distillation. A 4.5-ml aliquot was subjected to chromatography on a 1.7 × 10 cm column packed with alumina and the biphenyls were eluted with 200 ml of ether. Gas–liquid partition chromatography with G.E. SF-96 on firebrick was shown to separate known mixtures of bibenzyl and the three nitribiphenyls. Products of peak heights times the widths at one-half the heights obtained from known mixtures of the nitrobiphenyls in approximately the ratio found in the reaction mixture gave amounts relative to bibenzyl as an internal standard which were accurate to within about 10%. The ratio so obtained is presented in Table II.

Rate of Decomposition of N-Acetyldiphenyltriazene H/H-I in Benzene.—A solution of H/H-I in benzene was used to fill a number of tubes which were sealed and placed in a constant temperature bath maintained at 95.00 ± 0.05°. The bath temperature was determined with a thermometer which had been calibrated by the National Bureau of Standards. When the tubes were opened 15-μl aliquots were removed and diluted with 10 ml of cyclohexane. Initial use of eight absorbancies in the region from 310–345 mμ gave the same results as the determination of a single absorbance at 292 mμ so that the latter procedure was followed. Representative data are presented in Table V.

TABLE V

DECOMPOSITION OF N-ACETYL-N,N′-DIPHENYLTRIAZENE (H/H-I) IN BENZENE AT 95.00 ± 0.05°, C_0 0.0987 *M*

	A_{292}, mμ		10^5k_1, sec^{-1}	
t, 10^{-4} sec	1	2	1	2
0	0.725	0.657	...	...
1.08	.642	.594	1.13	0.93
2.52	.485	.469	1.60	1.34
4.32	.370	.368	1.56	1.34
6.12	.322	.302	1.33	1.27
10.80	.234	.185	1.05	1.17
		Av	1.33	1.21
		Av (10 points)	1.27[a]	

[a] With other initial concentrations the values of k_1 were 0.0226 *M*, 1.31 × 10^{-5}; 2.66 *M*, 1.25 × 10^{-5} sec^{-1}. The average of all data (20 points) was 1.27 × 10^{-5}. A fit with the analog computer of all of the data gave a value of 1.33 × 10^{-5} sec^{-1}.

Decomposition of CH_3O/Cl-I and Cl/CH_3O-I in Benzene.—These reactions were carried out at 95.00 ± 0.05° by the method employed for the unsubstituted compound H/H-I. Concentrations of the two isomeric N-acetyltriazenes were determined from the eight absorbancies of the reaction mixture at wavelengths taken at 5-mμ intervals over the range 310–345 mμ, *i.e.* at 310, 315, etc. Using the method of Dewar and Urch[14] plots of A/ϵ_1 *vs.* ϵ_2/ϵ_1 at the eight wavelengths (where A is the measured absorbancy of the reaction mixture and ϵ_1 and ϵ_2 are the extinction coefficients of components 1 and 2 respectively) gave straight lines with a slope c_2 and intercept c_1. Reactions were carried out in duplicate. Rate constants were obtained by plotting the disappearance of CH_3O/Cl/I and appearance and decay of the concentration of Cl/CH_3O-I in the reaction starting with CH_3O/Cl-I and in addition the comparable data for reactions starting with Cl/CH_3O-I. The analog computer was programmed[20] for the set of differential equations corresponding to the kinetic scheme assumed in the text. Potentiometer settings corresponding to the rate constants k_1, k_{-1}, k_a, and k_b were made in the way

$$d(A)/dt = -k_1(A) + k_{-1}(B) - k_a(A) \quad dP_a/dt = k_a(A)$$

$$d(B)/dt = -k_{-1}(B) + k_1(A) - k_b(B) \quad dP_b/dt = k_b(B)$$

giving the best fit to the curves (the same rate constants were used for the reactions with the starting material CH_3O/Cl-I as with those with starting Cl/CH_3O—only the initial concentration voltages were changed). One set of data is presented in Figure 1. The results are presented in Table III.

A reaction of 23.9 mg of Cl/CH_3O-I in 30 ml of benzene (shown by Dewar and Urch analysis to contain no CH_3O/Cl-I initially) was heated (divided between two sealed tubes) at 95.0° for 65 min. A Dewar and Urch analysis of a 0.16-ml aliquot diluted with 10.0 ml of benzene indicated that the solution contained 9.2 mg of CH_3O/Cl-I and 4.7 mg of Cl/CH_3O-I. The benzene was removed from the remaining solution by freeze drying at 1.5 mm for 24 hr to give 21.4 mg of product mixture. Repeated chromatography on sodium acetate washed silica gel G and eluting with 35:65 benzene–pentane led to the separation of a small amount of the rearranged isomer CH_3O/Cl-I, mp 141–141.5°, and shown by Dewar and Urch analysis to be 95% pure. From one of the tubes prepared as for the kinetic study and heated at 95.00° for 4320 min the benzene was distilled and the contents of the tube were dissolved in a few drops of acetonitrile. Chromatography on Eastman K 301R thin layer chromatography sheets separated the *p*-methoxybiphenyl and *p*-chlorobiphenyl (elution hexane). The appropriate spots were cut out and dissolved in 10.0 ml of ethanol and the amount of the biphenyl present determined from the ultraviolet absorption at 260 mμ (*p*-methoxybiphenyl, ϵ 20,900) and at 253 mμ (*p*-chlorobiphenyl, ϵ 22,400). A similar procedure gave the amounts of *p*-chloroacetanilide [λ_{max} 250 mμ (ϵ 21,300)] and *p*-methoxyacetanilide [λ_{max} 250 mμ (ϵ 16,600)]. Control analyses of known mixtures were carried out. Results are presented in Table VI.

TABLE VI

DETERMINATION OF RATIOS OF PRODUCTS OF THE DECOMPOSITION OF ACYLTRIAZENE CL/CH_3O-I[a]

Products	From reaction	Control mixture employed	Found
p-Chlorobiphenyl/ *p*-methoxybiphenyl	1.30, 1.35	2.26	2.13, 2.12
p-Methoxyacetanilide/ *p*-chloroacetanilide	1.47, 1.42	1.28	1.36, 1.39

[a] Total yield of the two anilides was estimated to be 96% of the theoretical and of the biphenyls 67%.

Rates of the Reactions of the Methoxy-, Methoxychloro-, and Methoxytrifluoromethyl-N-acetyltriazenes (CH_3O/H-I, H/CH_3O-I, CH_3O/Cl-I, Cl/CH_3O-I, CH_3O/CF_3-I, and CF_3/CH_3O-I).—The same eight wavelengths were employed using the method of Dewar and Urch[14] to calculate concentrations of acyltriazenes and rate constants were found with an analog computer as described for the methoxychlorotriazenes above. Results are presented in Table III.

Reaction of Benzenediazonium Fluoroborate with Potassium Phthalimide.—When 1.1 g of potassium phthalimide was added to a solution of 1.2 g of benzenediazonium fluoroborate in dimethylformamide (dried over molecular sieves) there was visible evolution of nitrogen within 1 min and development of a brown color. The dark brown reaction mixture which resulted was not further examined.

Registry No.—H/H-I, 5702-80-7; CH_3O/Cl-I, 10074-59-6; Cl/CH_3O-I, 10074-60-9; CH_3O/CF_3-I, 10074-61-0; CF_3/CH_3O-I, 10074-62-1; CH_3O/NO_2-I, 10074-63-2.

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[20] C. L. Johnson, "Analog Computer Techniques," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1963.