(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.

% trapping =

(change in galvinoxyl concentration)/2 ×

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$_2$O: 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.

I n 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

(1) This work was supported in part by the Petroleum Research Fund of the American Chemical Society.

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used. For this reason, most of our work was done with polycyclic aromatic sensitizers which did not give photoproducts under the conditions of our experiments. An added convenience is that they are sulfonated and retained in the aqueous layer during the hydrolysis by sulfuric acid of the benzophenone phenylimine and unreacted azide.

We found that triphenylmethyl azide does indeed undergo sensitized decomposition with loss of nitrogen in the presence of triphenylene in benzene solution when irradiated by a medium-pressure mercury vapor lamp. The only detectable products are benzophenone phenylimine and unreacted triphenylmethyl azide, which together account for >95% of starting material. No benzene-insoluble material was observed as long as degassed solutions were used.

We next attempted to determine the triplet energy of triphenylmethyl azide by using sensitizers of different triplet energies. The results are given in Table I.

Table I. Sensitized Photolytic Rearrangement of Triphenylmethyl Azide

Sensitizer	$E_T{}^a$	Solvent	% reaction[e]
None	. . .	Hexane	7
Benzene	83.0[b]	Benzene	12
Fluorene	67.6	Benzene	34
Triphenylene	66.6	Benzene	30
Phenanthrene	62.2	Benzene	28
Naphthalene	60.9	Benzene	35
Pyrene	48.7	Benzene	22
Anthracene	42[c]	Benzene	13
9,10-Dichloroanthracene	40[d]	Benzene	12

[a] Triplet energy. Except where otherwise noted, figures are from ref 11. [b] W. A. Noyes, Jr., and I. Unger, *Advan. Photochem.*, **4**, 49 (1966). [c] G. Porter and M. W. Windsor, *J. Chem. Phys.*, **21**, 2089 (1953). [d] S. P. McGlynn, T. Azumi, and M. Kasha, *ibid.*, **40**, 507 (1964). [e] Most figures are averages of two runs. Reproducibility was ±2% or better.

Acetophenone and benzophenone were also tried, but difficulty in separating the sensitizers and their photolysis products from the desired products made the yields too uncertain to be useful. A similar, though less serious, problem arises with anthracene and 9,10-dichloroanthracene, which underwent photodimerization and photodecomposition, respectively. Consequently, we cannot be completely certain that the per cent reaction for these two sensitizers differs significantly from that for benzene alone. It probably does, for the sensitizer must still absorb a large proportion of the incident light, and the per cent reaction should be substantially less than in benzene alone if there were no sensitized reaction. It is evident from Table I that triphenylmethyl azide has a low triplet energy, certainly below 48.7 kcal/mole, and perhaps below 40 kcal/mole. An attempt to determine the triplet energy directly by a study of phosphorescence failed because no emission spectrum could be observed. The phosphorescence spectrum may be beyond the limits (6000 Å) of the instrument used, or the triplet may decay predominantly by nonradiative processes.

Having established that triphenylmethyl azide can decompose *via* a triplet intermediate, we next considered whether the direct photolysis also involves a triplet. The fact that the products are qualitatively the same in

the direct and sensitized reactions is suggestive circumstantial evidence. In Table II the migration aptitudes of substituted phenyl *vs.* phenyl for a series of triarylmethyl azides in the triphenylene-sensitized reaction are recorded. These figures are all close to unity regardless of the electronic nature of the *para* substituent, as previously observed in the direct photolysis[3] but not in the thermal reaction.[2] This quantitative correspondence of products in the direct and sensitized photolyses constitutes further evidence that the direct photolysis involves excitation to a singlet azide followed by intersystem crossing to a triplet azide through which subsequent reaction occurs.

Table II. Migration Aptitudes in the Triphenylene-Sensitized Photolyses of Triarylmethyl Azides

X in p-XC$_6$H$_4$	% reaction	Migration aptitude,[a] p-XC$_6$H$_4$/C$_6$H$_5$
NO$_2$	30	1.07 ± 0.03
Cl	25	0.97 ± 0.02
CH$_3$	20	0.89 ± 0.05
OCH$_3$	29	1.11 ± 0.05
N(CH$_3$)$_2$	28	1.08 ± 0.02[c]
N(CH$_3$)$_2$[b]	28	1.12 ± 0.03[d]

[a] Corrected for the statistical preference for phenyl, and for acid-catalyzed rearrangement during work-up (see Experimental Section). Each figure is the average of three separate reactions with indicated average deviations, and each analysis the average of three determinations, except where otherwise noted. [b] Sensitized by phenanthrene. [c] Duplicate reactions. [d] Single reaction. Deviation is average deviation of three analyses.

Whether decomposition of the triplet azide occurs *via* a discrete triplet nitrene or is concerted with aryl migration is not completely settled. We favor a discrete nitrene, for there is no evidence that the *para* substituents which should be especially good at stabilizing an odd electron (nitro and dimethylamino) have any appreciable effect on the migration aptitude. There is no reason to expect participation by the migrating group where there is no energetic advantage to be gained from it. If participation by the migrating group were necessary for nitrogen loss, then the differences in ability to participate should be reflected in the migration aptitudes. That they are not is more easily reconcilable with a discrete nitrene intermediate. Rearrangement of this species should have a very low activation energy compared to rearrangement with nitrogen loss, so that little discrimination is to be expected even if its energy content is by this stage little more than is needed to bring about reaction. We are undertaking further studies which we hope will permit more precise descriptions of the intermediates.

Experimental Section

Triarylmethyl azides were prepared by the method of Saunders and Ware,[2] and purified by recrystallization from hexane and/or chromatography on neutral grade V alumina. Their properties were as follows: triphenylmethyl azide, mp 63–64° (lit.[2] 64–65°); (*p*-chlorophenyl)diphenylmethyl azide, mp 48.5–49.5° (lit.[2] 50–51°); diphenyl(*p*-nitrophenyl)methyl azide, mp 65–66° (lit.[2] 62.2–63.5°); diphenyl(*p*-tolyl)methyl azide, mp 48–49° (lit.[2] 48.5°); (*p*-dimethylaminophenyl)diphenylmethyl azide, mp 76–77° (lit.[2] 77–78°). As previously reported,[2] (*p*-anisyl)diphenylmethyl azide was an oil which failed to crystallize and showed some hydroxyl absorption in the infrared even after chromatography on alumina.

Sensitizers were commercial materials carefully purified by chromatography on alumina followed by sublimation and/or recrystallization.

Solvents. Hexane was spectro grade used without further purification. Benzene was reagent grade purified by the method of Hammond.[9]

Photolyses were performed on 10 ml of 3% by weight (0.07 M) solutions of the azides in benzene (except for a control run in hexane). In the sensitized reactions, sufficient sensitizer (0.05 to 0.5 g) was added to ensure that >95% of the light absorbed was absorbed by the sensitizer. All solutions were degassed with two freeze–pump–thaw cycles and sealed under vacuum in Kimex tubes. The samples were then photolyzed for 16 hr with a Hanovia 679A medium-pressure mercury vapor lamp (Engelhard Hanovia, Inc., Newark, N. J.), using a Pyrex filter to minimize direct photolysis of the azides. The work-up procedure was essentially that of Saunders and Caress,[3] except that the solution was added to the sulfuric acid at 155–160° at such a rate as to avoid accumulation of nonvolatilized benzene, and the ether extracts were neutralized with sodium bicarbonate solution (neutralization necessarily preceded extraction with the products from (p-dimethylaminophenyl)diphenylmethyl azide). Analysis was by gas chromatography on a 5 ft × 0.125 in. column of 3% Apiezon L on Chromosorb G at 230–245°.

Control Experiments. Corrections were made by the method of Saunders and Caress[3] to the migration aptitudes for the ca. 2% of acid-catalyzed rearrangement suffered by the unreacted azides during the work-up. The small yield of rearranged products from the treatment of the azides with acid (most of the product is triaryl-

carbinol) rendered independent determination of the migration aptitudes imprecise, so the figures of Tietz and McEwen[10] for the benzhydryl azides were used. They do not give a result for the p-dimethylaminophenyl group, and we therefore determined its migration aptitude to be approximately 10. Corrections ran 2–12%, mostly below 10%, of the observed migration aptitudes. In one photolysis of triphenylmethyl azide, 0.1 g of (p-nitrophenyl)-diphenylcarbinol was added as an internal standard. The mixture was worked up and analyzed as usual on a gas-chromatographic column calibrated with synthetic mixtures of benzophenone, triphenylcarbinol, and (p-nitrophenyl)diphenylcarbinol. Assuming no loss or decomposition of the internal standard, over 95% of the azide appeared as benzophenone plus triphenylcarbinol. Finally, photolysis of 0.1 g of benzophenone phenylimine in 10 ml of benzene resulted in no decomposition, as judged by a gas chromatogram showing a single peak corresponding to an authentic sample of the imine in retention time.

Attempted Study of Emission Spectra. Samples were prepared as described by Hammond.[11] Solutions containing 0.001 M triphenylmethyl azide in 3-methylpentane or 5:1 methylcyclohexane-isopentane gave clear glasses at 77°K. The light source was a 3130 mercury PEK lamp with a B and L monochromator. The detecting system consisted of a Jarrell–Ash scanning monochromator and a 1P28 RCA photomultiplier (good to 6000 A only). Neither fluorescent nor phosphorescent emission was observed.

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Reactions of Aryl(trichloromethyl)carbinols with Sulfur Nucleophiles. Formation and Proof of Zwitterionic Structure of Iminothiazolidinones

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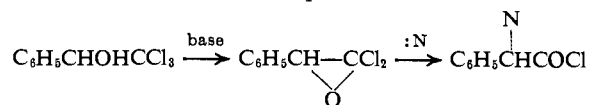
Abstract: Nucleophilic reagents react with aryl(trichloromethyl)carbinols to give α-substituted acids or derivatives. Thiourea is shown to act as a typical nucleophile in this reaction, with a subsequent ring closure giving an iminothiazolidinone. Thus, phenyl(trichloromethyl)carbinol is converted in one step to 2-imino-5-phenyl-4-thiazolidinone in 54% of the theoretical yield. This is a new approach to the synthesis of heterocyclic compounds. In like manner, 5-(3,4-dichlorophenyl)-2-imino-4-thiazolidinone and 2-imino-5-(p-methoxyphenyl)-4-thiazolidinone are obtained in yields of 28 and 18%, respectively. Nmr spectra, together with other evidence, allow the correct structure of the parent iminothiazolidinone to be chosen from the nine possible tautomeric forms. Potassium methyl xanthate also functions as a nucleophile in its reaction with phenyl(trichloromethyl)carbinol, but cyanide ion does not under the conditions employed. The relative nucleophilicities of the reagents tried are: thiourea ≫ xanthate > methoxide ≫ cyanide.

Phenyl(trichloromethyl)carbinol is known to react with methoxide ion in methanol to form α-methoxyphenylacetic acid,[2] and with potassium amide to form α-aminophenylacetic acid.[3] The reactions

are thought to take place *via* the following mechanism in which :N is the nucleophile.

$$C_6H_5CHOHCCl_3 \xrightarrow{\text{base}} C_6H_5CH\overset{\displaystyle -}{\underset{O}{CCl_2}} \xrightarrow{:N} C_6H_5\overset{N}{\underset{|}{CHCOCl}}$$

The acid chloride is converted under the basic reaction conditions to a salt of the α-substituted carboxylic acid.

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