5-Phenyltetrazole Photochemistry. A New Source of Phenylcarbene

PETER SCHEINER

Central Research Division Laboratory, Mobil Research and Development Corporation, Princeton, New Jersey 08540

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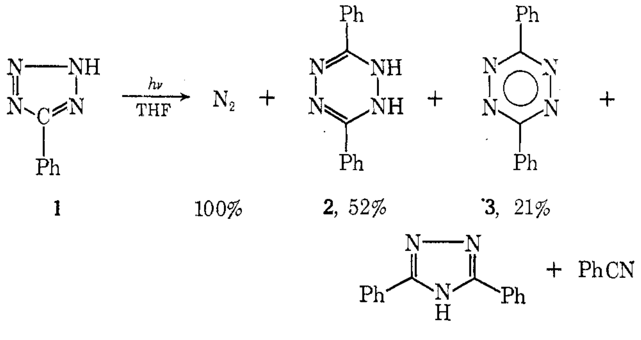
A product study of the photodecomposition of 5-phenyltetrazole (**1**) has been conducted. The results are compared with the corresponding thermolysis, and the photolysis of 5-phenyltetrazolide anion (**7**). Irradiation of **1** gives 1 equiv of nitrogen and a transient 1,3 dipolar intermediate. Dimerization of the latter to a dihydrotetrazine (**2**) comprises the major reaction path (>70%), but photolysis of **2** to benzonitrile and 3,5-diphenyl-1,2,4-triazole (**4**) also occurs. Though similar to thermolysis, the reaction is more selective. Photolysis of the anion (**7**) produces 2 equiv of nitrogen and products derived from the reaction of phenylcarbene with the solvent. Insertion (CH, OH, NH) and olefin addition products have been obtained. The method constitutes a new source of phenylcarbene, notable for its experimental simplicity. The reaction is believed to occur *via* phenyldiazomethane.

Despite growing interest in heterocycle photochemistry, limited information is as yet available concerning the behavior of several simple systems. In the polyaza series, the tetrazole–tetrazolide nucleus is notable. Three brief reports have dealt with the photolysis of 1,5-diphenyltetrazole[1a,2,3] and 1,5-dicarbomethoxytetrazole,[1b] and Huisgen's group has generated diphenylnitrile imine by photodecomposition of 2,5-diphenyltetrazole.[4] These studies, however, were not primarily directed toward the elucidation of tetrazole photochemistry. To this end, we chose to investigate the photolysis of 5-phenyltetrazole. The choice was dictated by two considerations—the thermal decomposition of this compound has been thoroughly examined,[5] thus providing a basis for comparison, and 5-phenyltetrazole affords the opportunity for contrasting the neutral molecule with the dissociated species, 5-phenyltetrazolide anion. Tetrazolide photochemistry has not been previously reported. The present paper describes the results of our product studies.

Results

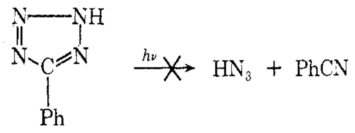
5-Phenyltetrazole.—The ultraviolet absorption spectrum of 5-phenyltetrazole (**1**) in ethanol exhibits a band centered at 239 mμ (ε 12,800), with more intense peaks at shorter wavelength.[6] Irradiation in the first absorption region by means of emission from a low-pressure mercury arc (254 mμ) caused the evolution of 1 equiv of nitrogen.[7] In deoxygenated methanol, the originally yellow photolysate solution gave, after extended reflux in air, 22% 3,6-diphenyl-1,2,4,5-tetrazine (**3**). The poor material balance suggested the presence of additional products. Further work was carried out in the nonhydroxylic solvent, tetrahydrofuran.



1 100% **2**, 52% **3**, 21% **4**, 8%

Irradiation in this solvent (0.165 *M*, 70 hr) produced the products in the isolated yields shown. A more prolonged run (98.5 hr) only slightly modified these results: 50% **2**, 23% **3** and 10% **4**. The initially obtained yellow product solution again indicated that 3,6-diphenyl-1,2,4,5-tetrazine (**3**), an intensely colored red-violet compound, was not present. It readily forms, however, by oxidation of **2** during work-up. The facile oxidation of **2** (and/or the 1,4-dihydro tautomer) has frequently been noted.[5,8] Thus 3,6-diphenyldihydrotetrazine (**2**) is formed in excess of 70%. This yield is about twice that found for thermolysis at 164°,[9] employing the same isolation procedure.

To facilitate identification, samples of **2**, **3**, and **4** were prepared by alternative routes. Comparison with authentic samples also revealed the absence of significant amounts of 2,4,6-triphenyl-*s*-triazine and 4-amino-3,5-diphenyl-1,2,4-triazole, compounds obtained in the thermal decomposition of **1**. Furthermore, hydrazoic acid, described by Huisgen and coworkers[9] as resulting from thermolysis, was not detected in the gaseous photolytic product. The lack of hydrazoic acid argued against photofragmentation of **1** to HN_3 and benzonitrile, and thus raised the question of the origin of the latter (as well as **4**; see Discussion).



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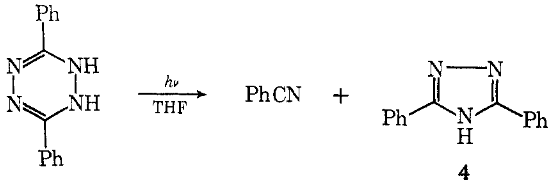
It appeared likely that benzonitrile derived from a secondary photoreaction of the major product (**2**).



2 **4**

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[1] (a) R. M. Moriarty and J. M. Kliegman, *J. Amer. Chem. Soc.*, **89**, 5959 (1967); (b) R. M. Moriarty, J. M. Kliegman, and C. Shovlin, *ibid.*, **89**, 5958 (1967).

[2] W. Kirmse, *Angew. Chem.*, **71**, 537 (1959).

[3] J. Sauer and K. K. Mayer, *Tetrahedron Lett.*, 325 (1968).

[4] J. S. Clovis, A. Eckell, R. Huisgen, and R. Sustmann, *Chem. Ber.*, **100**, 60 (1967).

[5] For leading references, see J. H. Markgraf, S. H. Brown, M. W. Kaplinsky, and R. G. Peterson, *J. Org. Chem.*, **29**, 2629 (1964).

[6] B. Elpern and F. C. Nachod, *J. Amer. Chem. Soc.*, **72**, 3379 (1950).

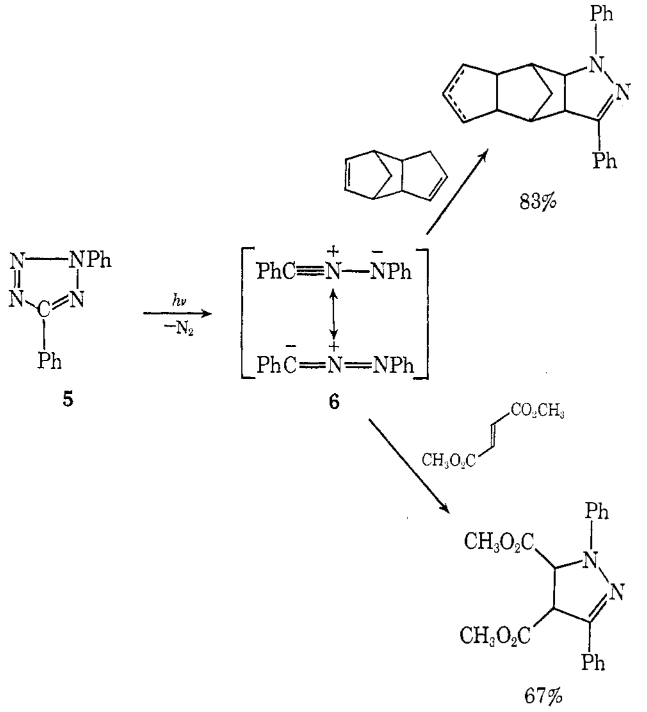
[7] $\Phi_{N_2} = 0.30 \pm 0.07$ in 2-propanol, at less than 10% reaction.

[8] E. Müller and L. Herrdegan, *J. Prakt. Chem.*, [2] **102**, 113 (1921).

[9] R. Huisgen, J. Sauer, and M. Seidel, *Ann.*, **654**, 146 (1962).

This supposition was confirmed by irradiating **2** in tetrahydrofuran. In an inefficient reaction, **2** was transformed to benzonitrile and 3,5-diphenyl-1,2,4-triazole (**4**). A 7% yield of **4** was isolated together with 84% recovered starting material (**2** + **3**) after 90 hr of irradiation. Other products were not detected.

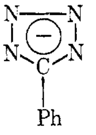
Though differing somewhat from thermolysis,[9] the results cited above are readily interpreted in terms of a 1,3-dipolar intermediate (see Discussion). Additional evidence for this type of intermediate was obtained by photolyzing 2,5-diphenyltetrazole **5** in the presence of dipolarophiles methyl fumarate and dicyclopentadiene. The anticipated adducts were formed in high yield, indicating the intermediacy of diphenylnitrile imine (**6**).[10,11]



5-Phenyltetrazolide.—While photolysis of 5-phenyltetrazole produced 1 equiv of nitrogen, an entirely different course of reaction occurred with the anion. Methanolic solutions of **1** containing 1 equiv of sodium methoxide, or solutions of preformed sodium 5-phenyltetrazolide, evolved 2 mol of nitrogen per mole of salt (**1** is acidic; pK_a 4.5 in 50% methanol.[12]) Unlike **1**, sodium 5-phenyltetrazolide is thermally stable in solution at 184°;[5] the solid is unchanged on heating at 325°. To enhance solubility in less polar media, further work was carried out with tetrabutylammonium 5-phenyltetrazolide (**7**).

Both the sodium and tetrabutylammonium salts display ultraviolet spectra similar to that of **1**. The long-wavelength maxima (ethanol) occur at 242 mμ (ε 14,100). Irradiations were therefore carried out at the same wavelength as those with 5-phenyltetrazole.

Following quantitative evolution of nitrogen, **7** afforded benzyl methyl ether (>90%) when irradiated in deoxygenated methanol. In water, benzyl alcohol was obtained, and benzyl *t*-butyl ether resulted in *t*-butyl alcohol solution. Analogously, photolysis of **7** in *t*-butylamine produced benzyl *t*-butylamine accompanied by a small amount of tributylamine. During the course of photolysis (methanol), the originally neutral 0.10 *M* solution became markedly basic, reaching a value of *ca.* pH 13 at the conclusion. Thus, the over-all stoichiometry in hydroxylic solvents may be represented by eq 1.



7

$$\overset{+}{N}(C_4H_9)_4 + 2ROH \xrightarrow{h\nu} 2N_2 + PhCH_2OR + RO^-\overset{+}{N}(C_4H_9)_4 \quad (1)$$

$$R = CH_3,\ C(CH_3)_3,\ H$$

Dissolved oxygen severly inhibited the reaction, an effect observed in methanol, *t*-butyl alcohol, and cyclohexane. Parallel runs in *t*-butyl alcohol, one purged with N_2, the other with O_2 prior to irradiation, illustrate the inhibition. (Solutions were irradiated together, equidistant from the source.) Nitrogen evolution from the deoxygenated run was 50% complete in 8 hr, while 6% of the theoretical volume resulted from the oxygen-saturated solution. After a prolonged period (*ca.* 18 hr), nitrogen evolution from the latter sharply increased. Benzyl *t*-butyl ether was the major product in either case.

Formal insertion into OH and NH bonds is characteristic of carbenes.[13] To explore the possible generation of phenylcarbene, **7** was irradiated in cyclohexane containing 1% methanol. Inclusion of methanol appeared advisable in view of the reaction stoichiometry; it also aided in solubilizing **7**. The analyzed products are shown in Table I. A small amount of higher molecular weight material was not characterized. On mechanistic grounds, cyclohexene and toluene may also have been formed.

TABLE I

PHOTOLYSES OF **7** AND *trans*-STILBENE OXIDE IN CYCLOHEXANE[a]

Product	Mole ratio[b] 7[c]	Mole ratio[b] *trans*-Stilbene oxide[c]
Benzylcyclohexane	4.75	4.46
Benzyl methyl ether	1.00	1.00
Bibenzyl	1.33	
Dicyclohexyl	0.33	0.60
Tributylamine	0.92	

[a] 1% methanol; 254 mμ, 35°. [b] Calibrated thermal conductivity detector. [c] Higher boiling material not analyzed.

The major product, benzylcyclohexane, may result from CH insertion, as described for phenylcarbene in cyclohexane.[14] Benzyl methyl ether arises from formal insertion into methanol. However, the unexpectedly large amount of bibenzyl (19% of the aromatic product) prompted comparison with an alternative method for generating phenylcarbene. Photolysis of *trans*-stilbene oxide, an excellent procedure developed by Griffin and

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[10] R. Huisgen, M. Seidel, G. Wallbillich, and H. Knupfer, *Tetrahedron*, **17**, 3 (1962).

[11] Photolytically generated **6** has been trapped with methyl crotonate.[4]

[12] R. M. Herbst and K. R. Wilson, *J. Org. Chem.*, **22**, 1142 (1957).

[13] J. Hine, "Divalent Carbon," The Ronald Press, New York, N. Y., 1964, pp 136–138.

[14] C. D. Gutsche, G. L. Bachman, and R. S. Coffee, *Tetrahedron*, **18**, 617 (1962).

coworkers,[15] was thus carried out under similar conditions. While CH and OH insertion again accounted for the bulk of the product (Table I), no bibenzyl was detected.

Tributylamine, found in this and other photolyses of **7**, suggests the transient presence of a strong base (eq 2).

$$(C_4H_9)_3\overset{+}{N}CH_2CH_2C_2H_5 + B \longrightarrow BH + n\text{-}C_4H_8 + (C_4H_9)_3N \quad (2)$$

Cyclopropane formation *via* carbene addition to olefins was investigated. The reaction was found to occur smoothly, and was notable for its experimental simplicity. The extent of reaction is readily gauged by the evolved nitrogen; work-up consists of water extraction to remove ionic materials. Cyclopropanes were identified by comparison with authentic samples prepared by *trans*-stilbene oxide photolysis. Reported nmr spectra[16,17] were valuable aids in assigning structures. Except as noted, the product distributions, *i.e.*, olefins and cyclopropanes from **7**, were similar to those from *trans*-stilbene oxide.

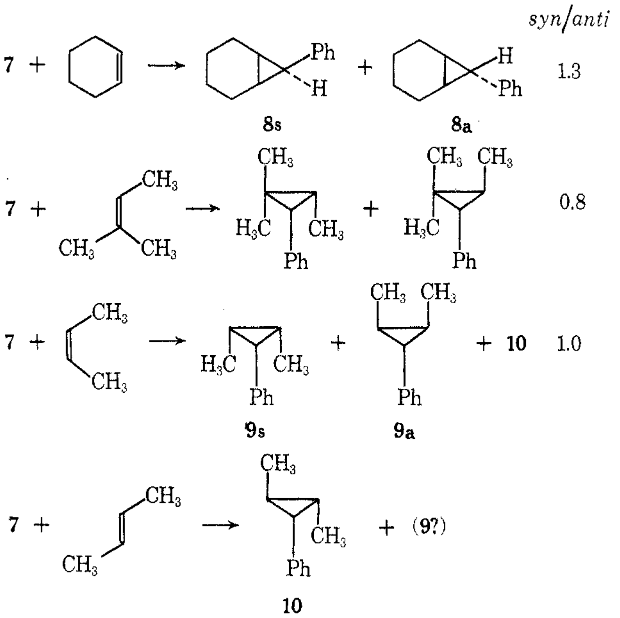
Approximately one-half of the C_{13} product with cyclohexene was cyclopropanes. The remainder consisted of mixed olefins, mainly 1-benzylcyclohexene. Analysis of the cyclopropanes showed both *endo*- (**8s**) and *exo*-7-phenylnorcarane (**8a**) in the ratio 1.3:1.0. The thermodynamically less stable *syn* epimer[17,18] was preferentially obtained, although these experiments (except runs with *cis*-2-butene) did not preclude photo-[19] or base-catalyzed isomerization. With *cis*-2-butene both isomers formed to about the same extent. The *syn*/*anti* ratio in this instance lies close to those reported for phenyldiazomethane[16] and *trans*-stilbene oxide[15a] photolyses (*ca.* 1.1). Scheme I summarizes the stereochemistry of cyclopropane formation from **7**.

Olefin geometry was predominantly preserved in the cyclopropanes from both *cis*- and *trans*-2-butene. However, a significant quantity of *trans* isomer (**10**) apparently resulted from the photolysis of **7** in *cis*-2-butene. In runs of varying duration, **10** comprised 6–10% of the cyclopropanes, while the *syn*/*anti* ratio was unaffected. Under identical conditions, only traces of **10** were observed using *trans*-stilbene oxide. (It must be noted that assignment of structure **10** from *cis*-2-butene rests on the vpc retention times on two dissimilar columns; 10% SE 30 and 10% Apiezon L. Experimental difficulties precluded isolation.) Overlapping olefin peaks in the gas chromatogram prevented unequivocal detection of the *cis* isomers in runs with *trans*-2-butene.

Discussion

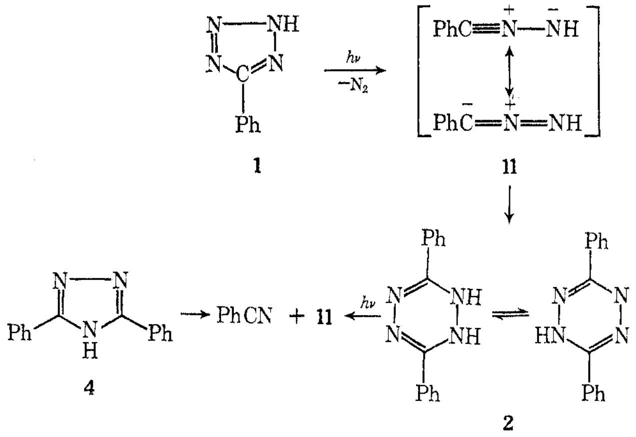
Huisgen, *et al.*,[9] have described 5-phenyltetrazole thermolysis in terms of two competing modes of fragmentation: (1) cleavage to hydrazoic acid and benzonitrile, and (2) expulsion of nitrogen with formation of the 1,3 dipole, C-phenylnitrile imine (**11**). The

SCHEME I

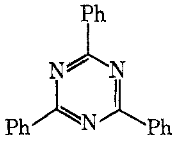


absence of hydrazoic acid and our observation of the photodecomposition of **2** to benzonitrile and **4** indicate that the photolysis of 5-phenyltetrazole occurs exclusively by the C-phenylnitrile imine (**11**) route. The products may be accounted for as shown in Scheme II.

SCHEME II



Dimerization of **11** produces the dihydrotetrazine **2**, presumably a tautomeric mixture.[9] Photolysis of **2** gives rise to **11** and benzonitrile, an efficient dipolarophile with nitrile imines.[9,20] Cycloaddition in the usual manner then gives **4**. In contrast to thermolysis, 2,4,6-triphenyl-*s*-triazine (**12**, benzonitrile trimer) and 4-amino-3,5-diphenyl-1,2,4-triazole (**13**) were not found among the photolytic products. These compounds



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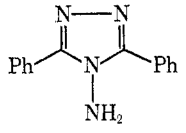

13

apparently result from thermal reactions requiring considerable activation energy. Photodecomposition of **2** to benzonitrile and 3,5-diphenyl-1,2,4-triazole (**4**)

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[15] (a) H. Dietrich, G. W. Griffin, and R. C. Petterson, *Tetrahedron Lett.*, 153 (1968). (b) H. Kristinsson and G. W. Griffin, *J. Amer. Chem. Soc.*, **88**, 1579 (1966); *Angew. Chem.*, **77**, 859 (1965).

[16] G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, **86**, 4042 (1964).

[17] F. R. Jensen and D. B. Patterson, *Tetrahedron Lett.*, 3837 (1966).

[18] Closs' designations are used:[16] **8s** = *syn*, **8a** = *anti*.

[19] W. von E. Doering and M. Jones, Jr., *Tetrahedron Lett.*, 791 (1963). However, see ref 15b concerning the photostability of the cyclopropanes in the present work.

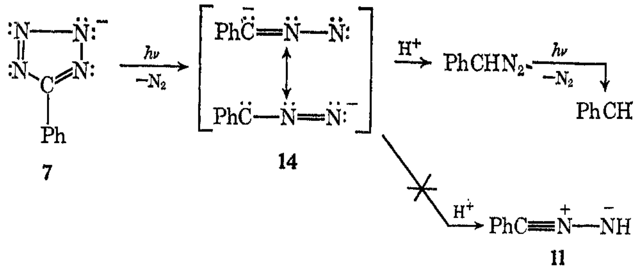
[20] R. Huisgen, M. Seidel, J. Sauer, J. W. McFarland, and G. Wallbillich, *J. Org. Chem.*, **24**, 892 (1959); R. Huisgen, R. Grashey, M. Seidel, G. Wallbillich, H. Knupfer, and R. Schmidt, *Ann.*, **653**, 105 (1962).

is the counterpart of a previously discussed thermal process.[9]

Photolysis of 5-phenyltetrazolide (**7**) leads to phenylcarbene. Quantitative expulsion of nitrogen and formation of characteristic insertion and addition products firmly support this conclusion. In view of the strikingly different decomposition paths found for 5-phenyltetrazole and its anion, it is of interest to consider possible routes to the carbene.

The close resemblance of the ultraviolet spectra of **1** and **7** (and 2-alkyl derivatives[6]) suggests similar electronic transitions in the 240–250-mμ region. As a working hypothesis, excitation of anion **7** might be considered to cause nitrogen expulsion in the manner of the tetrazole. Assuming formation of a spin-paired intermediate, C-phenylnitrile imine anion, *i.e.*, the anion of phenyldiazomethane (**14**), would result. Protonation of this base would follow (Scheme III).

SCHEME III

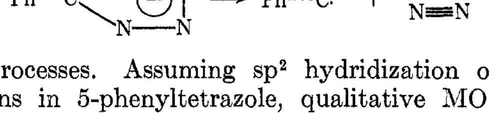


In 1934, Müller and Disselhoff[21] treated phenyldiazomethane with tritylsodium and presumably obtained **14**. But the properties of the salt were not explored. On the other hand, the parent nitrile imine, "isodiazomethane" (**15**), is rapidly and quantitatively

$$\underset{\mathbf{15}}{HC\equiv\overset{+}{N}-\overset{-}{N}H} \xrightarrow{KOH} CH_2N_2$$

tautomerized to diazomethane by base.[22] The isomerization proceeds through the corresponding anion of **15**.[22] Phenyldiazomethane itself is known to be stable in the presence of excess ethoxide.[23] Thus available evidence indicates that protonation of **14** would occur on carbon rather than nitrogen, giving rise to phenyldiazomethane. The lack of products derived from **11** accords with this expectation. Photochemically and thermally, phenyldiazomethane is a phenylcarbene precursor.

While alternatives, *e.g.*, eq 3, may be formulated, we find neither precedent nor theoretical justification for



(3)

such processes. Assuming sp² hydridization of the nitrogens in 5-phenyltetrazole, qualitative MO considerations indicate similar ground- and excited-state electron configurations for both **1** and **7**. It is therefore somewhat difficult to reconcile vastly differing modes of decomposition.

At relatively high concentrations, phenyldiazomethane decomposes to benzalazine, stilbenes, and products of the reaction of phenylcarbene with the solvent.[24] Absence of the former, bimolecular products may reflect the low steady-state concentration of phenyldiazomethane derived from **7**.

Phenylcarbene from **7** displays unusual chemical properties. Whereas the carbene from direct phenyldiazomethane photolysis adds stereospecifically to *cis*-2-butene,[16] we have found the addition to be somewhat nonstereospecific. The formation of an appreciable amount of bibenzyl (Table I) differs from earlier results[12,24] and from *trans*-stilbene oxide photolysis. Dietrich, Griffin, and Petterson[15a] have recently concluded that phenylcarbene formed photolytically from either phenyldiazomethane or *trans*-stilbene oxide reacts in the singlet state. The "discrepancies" observed in the present work suggest that a portion of the phenylcarbene undergoes reaction from the triplet state. Nonstereospecific addition to olefins has been used to characterize triplet carbenes,[25] and bibenzyl (dimerization of benzyl radicals) is an expected product of triplet phenylcarbene.[24] The origin of the presumed triplet phenylcarbene has not been determined. While relaxation to the triplet ground state[26] is possible, we favor partial photolysis of the intermediate phenyldiazomethane by triplet energy transfer. Work in progress may shed light on this question.

Experimental Section[27]

Photolysis of 5-Phenyltetrazole (1) in Tetrahydrofuran.—A solution of 2.900 g (19.84 mmol) of 5-phenyltetrazole[12] in 120 ml of anhydrous tetrahydrofuran was placed in a cylindrical quartz tube, purged with purified nitrogen for 0.5 hr, and irradiated[28] with stirring under nitrogen. Evolved gas (*ca.* 100%) was collected in a large Hg gas buret. After 70 hr the reaction was terminated. Passage of the gaseous product through 3 *N* silver nitrate produced no precipitate or turbidity, indicating the absence of hydrazoic acid.[29] The cloudy yellow photolysate was filtered, affording 0.160 g of white solid, mp 173–195°. Recrystallized from 50% ethanol, it had mp 216–217°, undepressed on admixture with **1**. The ir spectrum was identical with **1**.

The yellow filtrate was analyzed with slight modification by the procedure of Huisgen, *et al.*[9] Solvent was removed under reduced pressure and the residue was suspended in 30 ml of toluene. After 4 hr at −5°, the mixture was filtered and the residue was washed with a few milliliters of cyclohexane. Filtrate A was saved for further work (below). The residue was digested under nitrogen with 30 ml of 2 *N* sodium hydroxide for 30 min, then filtered, and washed with water. The resulting yellow crystalline solid, dried for 16 hr at 90° (120 mm), weighed 1.217 g (52%), mp 185–190° to a wine-red melt, as reported for **2**.[9] The ir spectrum (KBr pellet) was identical with authentic 1,2-dihydro-3,6-diphenyl-1,2,4,5-tetrazine's[9] (**2**). It had none of the peaks characteristic of 2,4,6-triphenyl-*s*-triazine (**12**) prepared by the method of Cook and Jones.[30] Acidification of the basic filtrate gave 20 mg of **4**.

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[21] E. Müller and H. Disselhoff, *Ann.*, **512**, 250 (1934).

[22] E. Müller and D. Ludsteck, *Chem. Ber.*, **87**, 1887 (1954).

[23] W. M. Jones and D. L. Muck, *J. Amer. Chem. Soc.*, **88**, 3798 (1966).

[24] For discussion, see D. Bethell and D. Whittaker, *J. Chem. Soc.*, *B*, 778 (1966).

[25] P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, **78**, 4496 (1956).

[26] R. W. Brandon, G. L. Closs, and C. A. Hutchison, *J. Chem. Phys.*, **37**, 1878 (1962); R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. A. Yeager, *J. Amer. Chem. Soc.*, **84**, 3213 (1962).

[27] Melting points are uncorrected. Nmr spectra were determined at 60 Mc with a Varian A-60 instrument, using TMS as an internal standard. Ir spectra were obtained with a Perkin-Elmer 237 spectrophotometer. Uv spectra were measured with a Cary 14 recording spectrophotometer. Vpc was carried out with an F & M 810 using helium as the carrier gas and a thermal conductivity detector.

[28] Unless otherwise noted, irradiations were conducted in a Rayonet chamber reactor using 16 8-W low-pressure Hg lamps (254 mμ, 35°).

[29] F. Feigl, *Rec. Trav. Chim. Pays-Bas*, **58**, 476 (1939).

[30] A. Cook and D. G. Jones, *J. Chem. Soc.*, 278 (1941).

A 1.000-g sample of product **2** and 2.33 g of sodium nitrite were stirred with 50 ml of ethanol at 50–60°. Dropwise addition of 36 ml of 2 *N* sulfuric acid caused precipitation of a red-violet solid. After 3 hr the mixture was diluted with 175 ml of ice–water, filtered, and dried at 90° (120 mm) for 12 hr. Pure 3,6-diphenyl-1,2,4,5-tetrazine (**3**, 0.958 g) was obtained, mp 195–197° (lit.[8] mp 195°).

Filtrate A (above) was extracted with four 12-ml portions of 2 *N* sodium hydroxide and the combined extracts were acidified with concentrated hydrochloric acid. Organic phase B was saved for further work (below). The white precipitate was collected, dried 12 hr at 90° (120 mm), and shown to be 3,5-diphenyl-1,2,4-triazole[9] (**4**) by ir comparison and melting point. The yield of **4** was 0.168 g (8%), mp 189–190° (lit.[31] mp 190°). Organic phase B was extracted with four 12-ml portions of 3 *N* hydrochloric acid, and the extract made basic with 50% sodium hydroxide solution. Organic phase C was saved for further work (below). Filtration gave, after drying, 0.122 g of red solid. This material was shown to be **3** contaminated with **2** by ir spectroscopy. Ir comparison with authentic 4-amino-3,5-diphenyl-1,2,4-triazole[9] (**13**) showed that this compound was not present.

Organic phase C (above), dried ($MgSO_4$) and evaporated under reduced pressure, gave an oily red solid smelling of benzonitrile. It was stirred with 10 ml of pentane and the pentane extract was decanted and concentrated to about 1 ml. Ir of the pentane solution showed the presence of benzonitrile (2222 cm^{-1}), as did vpc analysis (10-ft 10% Apiezon L, 170°). The red residue, dried at 100° (120 mm) for 16 hr, was essentially pure **3** (ir), yield 0.309 g (13%).

Photolysis of 1,2-Dihydro-3,6-diphenyl-1,2,4,5-tetrazine (2).—A solution of 1.150 g (4.87 mmol) of freshly prepared[9] **2** in 120 ml of tetrahydrofuran was irradiated for 75 hr and analyzed as described for **1**. In the first few hours the solution became orange-red, but it returned to the initial yellow color after 24 hr irradiation. The following products were isolated: **2** (64%), **3** (20%), **4** (7%). Benzonitrile was identified as described above.

Photolysis of 2,5-Diphenyltetrazole (5) with Dimethyl Fumarate.—A solution of 1.0 g (4.5 mmol) of **5**[32] and 8.0 g of dimethyl fumarate in 150 ml of ethyl acetate was irradiated in a quartz tube for 35 hr. Removal of volatile material (100°, 1 mm) gave 2.2 g of viscous product that crystallized on treatment with a few milliliter of methanol. Recrystallization from methanol gave 1.0 g (67%) of *trans*-4,5-dicarbomethoxy-1,3-diphenyl-Δ^2-pyrazoline, yellow plates, mp 150–151° (lit.[10] mp 149.5–151°). A similar run with dimethyl maleate and **5** gave the same product.

Photolysis of 2,5-Diphenyltetrazole (5) in Dicyclopentadiene.—A solution of 0.42 g (2.0 mmol) of **5** in 40 ml of commercial α-dicyclopentadiene was irradiated for 23 hr. Removal of the solvent under reduced pressure and crystallization of the residue (ethanol) gave 0.54 g (83%) of 1,3-diphenyl-4,8-methane-3a,4,-4a,7a,8,8a-hexahydroindeno[5,6-*c*]pyrazole, mp 172–174° (lit.[10] mp 173–174°).

Tetrabutylammonium 5-Phenyltetrazolide (7).—To 5.794 g (39.64 mmol) of **1** in 100 ml of methanol was added 38.5 ml (39.6 mmol) of 1.03 *M* tetrabutylammonium hydroxide in methanol. After 20 min the colorless solution was evaporated to give a quantitative yield of **7**, mp 128–131°. Four recrystallizations from ethyl acetate–hexane (3:1) gave the analytical sample, mp 134–135°.

Anal. Calcd for $C_{23}H_{41}N_5$: C, 71.27; H, 10.66; N, 18.07. Found: C, 71.44; H, 10.68; N, 18.10.

Photolyses of Tetrabutylammonium 5-Phenyltetrazolide (7). General Procedure.—Solutions of **7** (0.08–0.03 *M*, 120 ml in cylindrical quartz tubes) were purged with purified nitrogen for 0.5 hr and then irradiated with stirring under nitrogen. Methanol (1.0–2.0 g) was included in runs with hydrocarbon solvents. Except for cyclohexane, the initial hydrocarbon solutions were not completely homogeneous. All irradiations were carried to greater than 65% reaction (21–52 hr) as determined by gas evolution. Products were isolated from hydrocarbon solutions by washing the photolysate with 30-ml portions of water until the aqueous was neutral to pH paper. Four such extractions were usually sufficient. The organic phase was dried ($MgSO_4$) and the solvent evaporated. The resulting oils were analyzed by vpc, and the products were collected for ir and nmr analysis. Vpc employed 10-ft, 10% SE 30 on Chromosorb W and 4-ft, 10% Carbowax on Chromosorb W columns at appropriate temperatures. Quantitative data were obtained with a disk integrator. The detector response was calibrated with an accurately weighed known mixture of the products for the run in cyclohexane (Table I).

Water-soluble photolysate solutions were first concentrated to a few milliliters under reduced pressure, then taken up in ether (40 ml), and extracted with water as above.

Runs with *cis*- and *trans*-2-butene were carried out by condensing (−78°) about 40 ml of the olefin, 1.0 g of **7**, and 1.0 g of methanol in a cylindrical Vycor tube fitted with a pressure cap. Irradiation without stirring was conducted in a large water bath (18–22°) with an immersed 450-W (Hanovia, Type A) medium-pressure mercury arc.

Authentic samples of the cyclopropanes and benzylcyclohexane were prepared by the method of Griffin and coworkers.[15b] Benzyl *t*-butyl ether was prepared in low yield (18%) by heating 0.03-mol portions of benzyl chloride and potassium *t*-butylate in 40 ml of *t*-butyl alcohol for 45 hr. The ether was isolated by preparative vpc and characterized by its ir and nmr spectra. All identified products were isolated (vpc) and compared with genuine samples (ir, nmr, vpc retention time).

Registry No.—**1,** 18039-42-4; **2,** 14478-73-0; **3** 6830-78-0; **4,** 2039-06-7; **5,** 18039-45-7; **7,** 12310-17-7.

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[31] R. Stolle, *J. Prakt. Chem.*, [2] **69**, 145 (1904).

[32] R. Huisgen, J. Sauer, and M. Seidel, *Chem. Ber.*, **94**, 2503 (1961).