

The normal precautions used in handling moisture-sensitive acid chlorides should be exercised. Both racemic and optically pure (6) acid chlorides were prepared by this method.

O-Methylmandelamides were prepared by reaction of the appropriate amine in benzene with a solution of O-methylmandelyl chloride in benzene containing an excess of pyridine. The reaction mixture was allowed to stand at room temperature for 30 min and then poured into a separatory funnel containing ether and water. The ether layer was washed successively with dilute aqueous hydrochloric acid, dilute aqueous sodium bicarbonate, and water. The ether layer was dried over anhydrous magnesium sulfate, filtered, and the solvent was removed under reduced pressure to yield the crude mandelamide. The mandelamides thus obtained were sufficiently pure for examination by nmr spectroscopy.²⁹ Analytical samples were crystallized from benzene-petroleum ether (bp 30–60°) mixtures. Nmr properties of the amides and menthyl O-methylmandelate (which was prepared in the same manner) are given in Table I and the text.

(-)-N-[1-(1-Naphthyl)ethyl]-O-methylmandelamide (7), prepared from 1 and optically pure (*R*)-O-methylmandelyl chloride (6), had mp 132–133°, $[\alpha]_D^{25} -24^\circ$ (*c* 1.59, ethanol).

Anal. Calcd for C₂₁H₂₁NO₂: C, 78.96; H, 6.63; N, 4.39. Found: C, 78.91; H, 6.55; N, 4.29.

(+)-N-Methyl-N-[1-(1-naphthyl)ethyl]-O-methylmandelamide

(29) An nmr spectrum of the crude material should be run prior to any purification in order to ascertain that the ratio of diastereomers is not altered during this procedure.

(8), prepared from 2 and 6, had mp 93–95°, $[\alpha]_D^{25} +33^\circ$ (*c* 0.91, ethanol).

Anal. Calcd for C₂₂H₂₃NO₂: C, 79.25; H, 6.96; N, 4.20. Found: C, 79.26; H, 6.85; N, 4.10.

N-[(1-Methyl-2-phenyl)ethyl]-O-methylmandelamide was a diastereomeric mixture (*ca.* 1:1) prepared from racemic amine and racemic O-methylmandelyl chloride and recrystallized three times to mp 59–60°.

Anal. Calcd for C₁₈H₂₁NO₂: C, 76.30; H, 7.47; N, 4.94. Found: C, 76.52; H, 7.73; N, 4.66.

N-(1-Phenylethyl)-O-methylmandelamide was a diastereomeric mixture (*ca.* 1:1) prepared from racemic amine and racemic O-methylmandelyl chloride and recrystallized three times to mp 132–137°.

Anal. Calcd for C₁₇H₁₉NO₂: C, 75.80; H, 7.11; N, 5.20. Found: C, 75.57; H, 7.00; N, 5.26.

Menthyl O-methylmandelate was prepared from an excess of (-)-menthol and racemic O-methylmandelyl chloride. The mixture of diastereomers (*ca.* 1:1) had bp 85° (0.15 mm).

Anal. Calcd for C₁₉H₂₃O₃: C, 74.97; H, 9.27. Found: C, 74.74; H, 9.11.

Registry No.—2, 15297-33-3 3, 15297-34-4; 4, 15297-35-5; 5, 15297-36-6 7, 15297-37-7 8, 15314-01-9; N-[(1-methyl-2-phenyl)ethyl]-O-methylmandelamide, 15297-38-8; N-(1-phenylethyl)-O-methylmandelamide, 17296-90-9; menthyl-O-methylmandelyl, 15296-91-0.

Carbene Reactions from a Diazomethyltriazole. Contrast with the Isosteric Azide¹

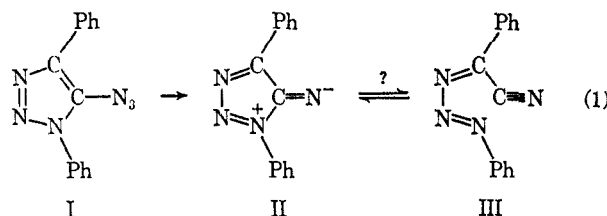
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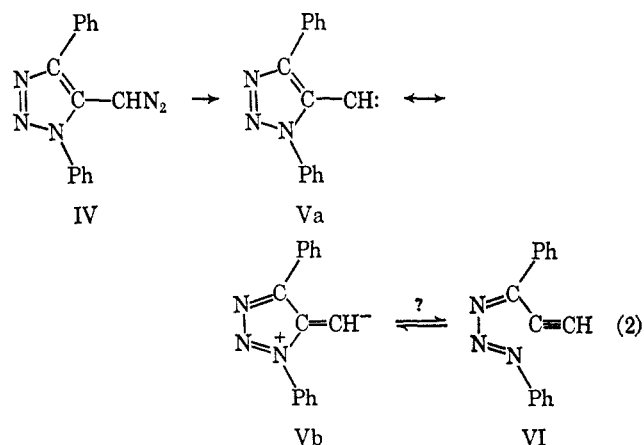
Because 5-azido-1,4-diphenyltriazole loses nitrogen to form an isolable substance that may be an electronically stabilized nitrene, the isosteric diazoalkane was prepared and examined for analogous behavior. No isolable primary decomposition product could be obtained. The crystalline diazo compound lost nitrogen smoothly above 40° without catalysis, attacking the solvent (benzene, cyclohexane, cyclohexene, carbon tetrachloride) to give typical products of carbene insertion or addition in unusually high yields (70%). Decomposition had nearly the same rate in all the hydrocarbon solvents, but was autocatalytic in carbon tetrachloride. The selectivity toward the hydrocarbon solvents was 25:2.1:1 cyclohexene, benzene, and cyclohexane, respectively; the ratio of addition to insertion in reaction with cyclohexene varied from 7.7 to 11. The position isomer, 4-diazomethyl-1,5-diphenyltriazole, lost nitrogen to form a mixture of the corresponding aldzine and the anil of phenyl ethynyl ketone, without detectable attack on any solvent.

We recently reported² on the unusual behavior of an azide, 1,4-diphenyl-5-azidotriazole (I), which loses nitrogen from the azido group at relatively low temperatures and forms a product in which neither rearrangement, cyclization, intermolecular insertion, nor hydrogen abstraction have occurred. The structure of this substance, which might be considered as an electronically stabilized nitrene (imidogen), was narrowed down to two possibilities (II and III); its behavior was most readily accounted for by assuming an active equilibrium between the two in solution (eq 1).



(1) From the Ph.D. Dissertation of J. G. W., Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, p 1620.

The isosteric carbon system, namely, 5-diazomethyl-1,4-diphenyltriazole (IV), became of obvious interest because of the possibility of isolating a substance that might be considered as an electronically stabilized carbene (V) (eq 2), which would bear some analogy to

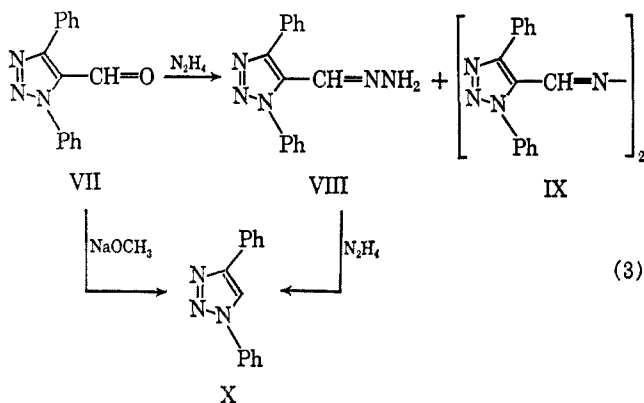


(2) P. A. S. Smith, L. O. Krbecek, and W. Resemann, *J. Amer. Chem. Soc.*, **86**, 2025 (1964).

isocyanides and to the compound isolated by Wanzlick.³ Furthermore, the investigation of such a system might shed additional light on the importance of the equilibria $\text{II} \rightleftharpoons \text{III}$ and $\text{V} \rightleftharpoons \text{VI}$. The question of whether the species initially formed might exist as a triplet carbene distinct from Va, perhaps able to show individual behavior as an ordinary, "unstabilized," carbene before transformation to V or VI, was also of much interest.

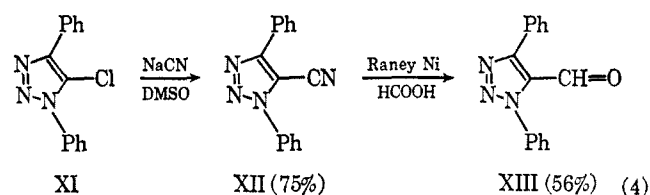
Results

5-Diazomethyl-1,4-diphenyltriazole (IV) was prepared by converting the 5-carboxaldehyde VII into its tosylhydrazone and treating that with butyllithium. The product could be obtained analytically pure as orange crystals, although with some difficulty and concomitant losses (in some experiments it was convenient to utilize the unisolated diazo compound in solution). Several other routes to this substance were tried, but none succeeded except oxidation of the unsubstituted hydrazone, VIII, with mercuric oxide. However, not only was the oxidation highly irreproducible, but the preparation of the hydrazone from the aldehyde was beset with two serious side reactions: formation of the aldazine (IX) and decarbonylation to form 1,4-diphenyltriazole (X). The latter reaction was demonstrated to be a nucleophilic cleavage, analogous to the well-known example of chloral, and could be accomplished quantitatively by treating the hydrazone with excess hydrazine or the aldehyde with sodium methoxide (eq 3).

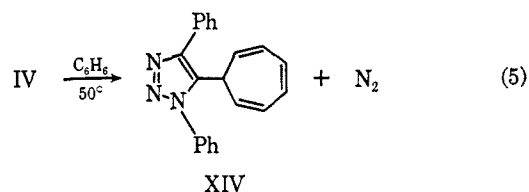


The preparation of the required 1,4-diphenyltriazole-5-carboxaldehyde (VII) from phenylpropionaldehyde and phenyl azide⁴ also gave a supply of the isomer 1,5-diphenyltriazole-4-carboxaldehyde. This aldehyde was insensitive to nucleophilic deformylation, in contrast to the other isomer. The position isomer of IV, 4-diazomethyl-1,5-diphenyltriazole, was obtained from this aldehyde in good yield with consistent success by conversion into the hydrazone and oxidation with mercuric oxide or activated⁵ manganese dioxide, in marked contrast to the analogous route to IV. When IV alone was wanted, there was some advantage in synthesizing the 5-carboxaldehyde

by Raney nickel-formic acid reduction⁶ of 5-cyano-1,4-diphenyltriazole, obtained by reaction of the 5-chloro compound with sodium cyanide in dimethyl sulfoxide (eq 4).



The diazomethyltriazole IV lost nitrogen readily in benzene solution at 50° (eq 5). Vapor phase chroma-



tography revealed no volatile products, but column chromatography on alumina produced, besides some tar, a small amount (8%) of the corresponding aldazine and one other product (66%) whose analysis corresponded to loss of two atoms of nitrogen and addition of the elements of benzene. It added bromine, reduced neutral permanganate, and formed an adduct with maleic anhydride. The nmr spectrum (triplet, 1 H, at τ 6.87; quartet, 2 H, at 4.68; multiplets at 3.77 2 H and 3.40 2 H; and a complex multiplet, 10 H, centered at 2.5) was quite similar to that of cycloheptatriene.⁷ The presence of six hydrogens at low field (τ 3.40–4.68) is not consistent with a norcaradiene structure, in which the two equivalent cyclopropane hydrogens would be expected to resonate near 6.5 or higher (*cf.* 7,7-dicyanonorcaradiene⁸). The product is thus presumably 7-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene (XIV). Decomposition of IV in more dilute solution (0.005 M) produced none of the azine formed in the more concentrated solution. When oxygen was bubbled through the solution of decomposing IV, the corresponding aldehyde was obtained in only 3% yield in addition to the other products. When carbon monoxide was used instead of oxygen, the products could not be cleanly separated, but the observation of strong bands at 1740 and 1660 cm^{-1} in the infrared spectrum of the residue from the reaction indicated that some carbonyl products had been formed, presumably *via* a ketene initially formed by reaction with the carbon monoxide.

Decomposition of IV in cyclohexane gave some tar, the aldazine (IX) (14%), and a major product (67%) corresponding to loss of two atoms of nitrogen and addition of the elements of cyclohexane. The nmr spectrum (multiplets, 11 H, at τ 9.1 and 8.6; doublet, 2 H, at 7.25; complex multiplet, 10 H, centered at

(3) H. W. Wanzlick and E. Schikora, *Angew. Chem.*, **72**, 494 (1960); D. M. Lemal, R. A. Lovald, and K. I. Kawano, *J. Amer. Chem. Soc.*, **86**, 2518 (1964).

(4) J. C. Sheehan and C. A. Robinson, *ibid.*, **73**, 1207 (1951).

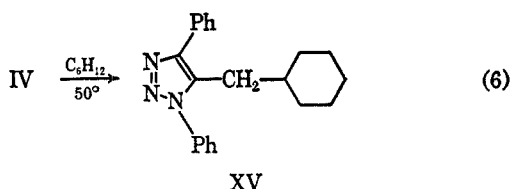
(5) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952); E. F. Pratt and J. F. Van DeCastle, *J. Org. Chem.*, **26**, 2973 (1961).

(6) O. G. Backeberg and B. Staskun, *J. Chem. Soc.*, 3961 (1961).

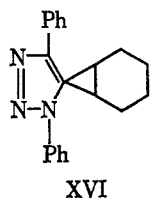
(7) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 158.

(8) E. Ciganek, *J. Amer. Chem. Soc.*, **87**, 652, 1149 (1965); *cf.* also J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *ibid.*, **87**, 3896 (1965).

2.5) corresponded with the structure 1,4-diphenyl-5-cyclohexanemethyltriazole (XV) (eq 6).



In cyclohexene solution at 50°, IV gave rise to a reaction mixture that was not readily resolved by thin layer chromatography, in which it showed R_f values similar to that of XV. The mixture was therefore hydrogenated to saturate the presumed cyclohexenyl groups, and then chromatographed on silica gel, which, however, accomplished only partial separation into two components, mp 143–151° and 127–132°, respectively, in a total yield of 78%. Several recrystallizations of each converted the lower melting fraction into pure XV, and the other fraction into an isomeric compound, mp 150–153°, which reacted sluggishly with bromine and not at all with permanganate. The infrared and nmr spectra were consistent with a triazolynorcaradiene structure (XVI); this as-



signment was confirmed by the formation of the same substance by hydrogenation of the triazolylcycloheptatriene, XIV. The ratio of XVI to XV in the reaction mixture was estimated as 7.7:1 from the nmr spectrum before chromatography.

The selectivity of attack on the solvents benzene, cyclohexane, and cyclohexene was determined from yields of products from reactions carried out in mixed solvent pairs. From a solution of IV (0.01 *N*) in an equimolar mixture of benzene and cyclohexane, a ratio of XIV (attack on benzene) to XV (attack on cyclohexane) of 2.10 ± 0.05 was obtained by three different methods of estimation. From an equimolar mixture of benzene and cyclohexene, a ratio of XVI (attack on cyclohexene) to XIV of 9 ± 1.5 was obtained. The third solvent combination, cyclohexene and cyclohexane, was used in a mole ratio of 1:10 owing to the large anticipated difference in susceptibility to attack. A ratio of XVI to XV of 2.5 ± 0.5 was estimated from the nmr spectrum of the mixed products; correction for the mole ratio of the solvents leads to a selectivity of 25 ± 5 for cyclohexene-cyclohexane. A further correction for the amount of insertion products (tetrahydrobenzyltriazoles) also formed from cyclohexene (1 part in 8.7) would raise this ratio to about 28.

Two fluorinated solvents were tried in an effort to find an inert medium for the decomposition of the diazo compound IV. Perfluorodioxane did not appear to dissolve significant quantities of IV; heating a vigorously stirred suspension at 60° produced only the corresponding aldazine (76%). Perfluorobenzene dissolved IV satisfactorily. Heating a solution of IV

in it produced only tars, from which no pure substance could be obtained. The residue from evaporation of the solvent contained no detectable fluorine, indicating that the tars did not derive from attack on the solvent.

Attempted decomposition of the melted diazo compound IV (under nitrogen) resulted in mild explosions and the formation of tarry residues, from which a small amount of the aldazine was the only pure compound that could be isolated.

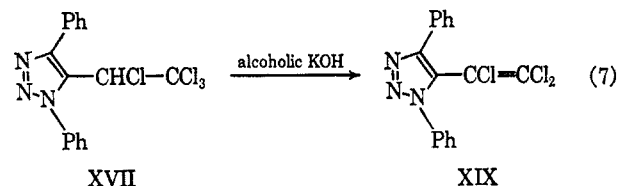
Rates of decomposition of IV were determined by following its disappearance spectroscopically. The rates at 50° in cyclohexene, in benzene, and in mixtures of cyclohexane with ether or benzene were first order (the solubility and rate of solution of IV in neat cyclohexane were too low to give satisfactory results). The rate constants obtained are given in Table I. A rate constant for benzene solutions was also determined at 40°, allowing an approximate value of the activation energy, 26 kcal/mol, to be estimated.

TABLE I
FIRST-ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF
1,4-DIPHENYL-5-DIAZOMETHYL-1,2,3-TRIAZOLE (IV)

Solvent	Temp, °C	$10^4 k$, min ⁻¹
Cyclohexene	50.0	17.6
Benzene	50.0	9.2
Benzene	40.0	2.5
Cyclohexane-ether (2:1 mole ratio)	50.0	17.1
Cyclohexane-benzene (equimolar)	50.0	19.3
Cyclohexane-benzene (2:1 mole ratio)	50.0	19.8

The rate of decomposition of IV in carbon tetrachloride solution did not obey either first-order or second-order kinetics over-all. It accelerated rapidly at first, and became first order only in the latter part of each run, from which a rate constant of 122×10^{-3} min⁻¹ could be determined.

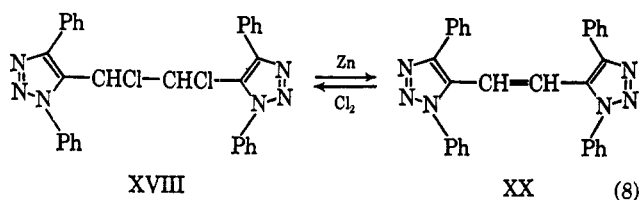
The products, as well as the kinetics, were different in carbon tetrachloride. In addition to small amounts of hexachloroethane, chromatography separated two colorless, crystalline chlorine-containing compounds (XVII and XVIII) in substantial amounts. Compound XVII, $C_{16}H_{11}N_3Cl_4$, had an infrared spectrum that showed general resemblance to spectra of other 1,4-diphenyltriazole derivatives; its nmr spectrum showed an aromatic multiplet centered at τ 2.5 (10 H) and a singlet at 4.22 (1 H). Treatment with alcoholic potassium hydroxide (see eq 7) produced a new compound, XIX, $C_{16}H_{10}N_3Cl_3$, whose infrared



spectrum showed a new band at 1625 cm⁻¹, attributable to C=C stretching; the singlet at τ 4.22 in the nmr spectrum was no longer present. XVII is thus presumed to be 1,4-diphenyl-5-(1,2,2,2-tetrachloroethyl)-1,2,3-triazole, and XIX, the 5-trichlorovinyl analog.

Compound XVIII, $C_{30}H_{22}N_6Cl_2$, had an infrared spectrum similar to XVII, but was too insoluble to give a satisfactory nmr spectrum. Treatment with

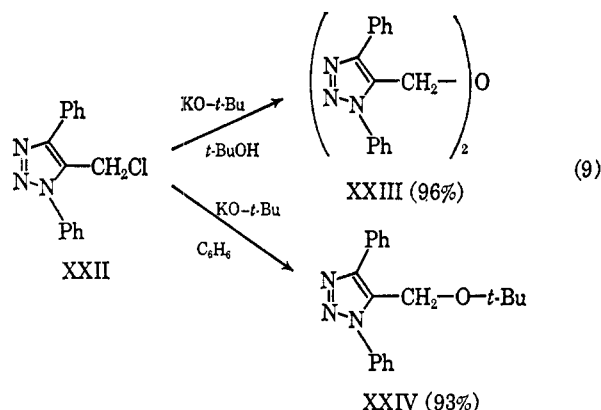
zinc dust removed the chlorine atoms, producing 1,2-bis(1,4-diphenyl-1,2,3-triazol-5-yl)ethylene (XX), which was converted back into XVIII by treatment with chlorine (eq 8). The structure shown for XVIII,



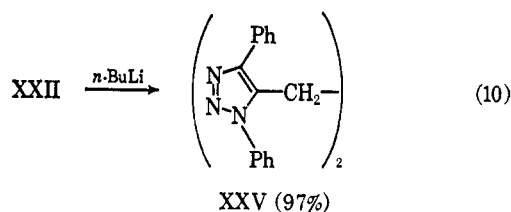
with uncertain stereochemistry, is consistent with the observations. (A small amount of a high-melting crystalline compound, $C_{30}H_{22}N_6O_3Cl$, which may have been an artifact of the work-up, was also obtained both from the original reaction and from the treatment of XX with chlorine; it was too insoluble to give an nmr spectrum, and was not further investigated.)

Photolysis of the diazomethyl triazole IV was carried out at 10° , at which temperature thermal decomposition was determined to be negligibly slow. The results were essentially the same as in thermal decomposition. In benzene, XIV was produced in 69% yield, and in cyclohexene the ratio of product from addition to those from insertion was 11.5:1 (combined yield 62%). No reaction with molecular oxygen could be detected in experiments performed with or without the presence of benzophenone as sensitizer.

Some alternative routes were explored for producing the same carbene as is presumably formed from the diazomethyl compound. Dehydrohalogenation of 1,4-diphenyl-5-chloromethyl-1,2,3-triazole (XXII) with potassium *t*-butoxide failed. In *t*-butyl alcohol solution, the principal product was the symmetrical triazolomethyl ether (XXIII) (eq 9), whose structure

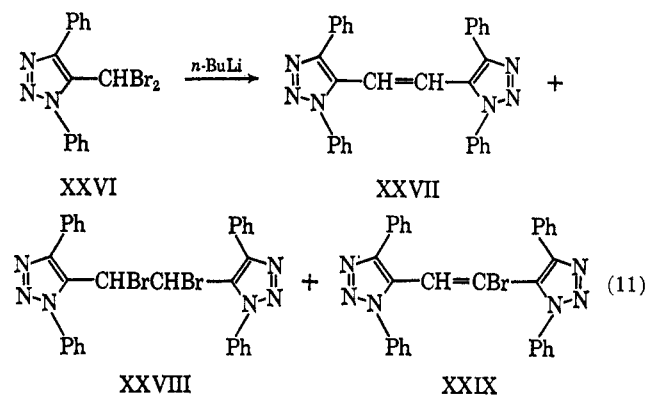


was deduced from its analysis, molecular weight, infrared spectrum (strong C-O-C band at 1060 cm^{-1}), and nmr spectrum (singlet, 2 H, at τ 5.42, and aromatic multiplet, 10 H, centered at 2.5). With dry potassium *t*-butoxide suspended in benzene, the product was the *t*-butyl ether (XXIV) (eq 9), which had a similar infrared spectrum, but whose nmr spectrum showed singlets at τ 8.74 (9 H) and 5.62 (2 H) in addition to the aromatic multiplet (10 H). *n*-Butyllithium produced as the sole product a compound $C_{30}H_{24}N_6$ (eq 10), whose nmr spectrum (singlet, 4 H,



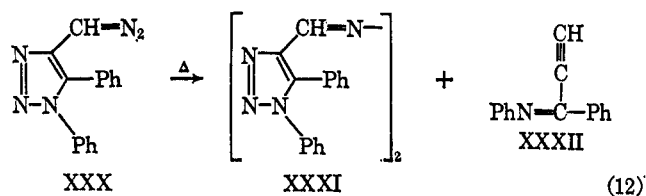
at τ 7.03 aromatic multiplet, 20 H, centered at 2.6) was consistent with with *sym*-bis(1,4-diphenyltriazol-5-yl)ethane (XXV). This is the product to be expected of halogen-metal interchange followed by reaction of $ArCH_2Li$ with $ArCH_2Cl$.

Dehalogenation of the corresponding dibromomethyl compound (XXVI) with *n*-butyllithium (eq 11) was



attempted in a variety of solvents. Essentially the same product mixture was always obtained; the products were of the same type as has been reported for other *gem*-dihalides, and presumably did not arise *via* a carbene intermediate. The major component (54%), $C_{30}H_{22}N_6$, gave normal olefinic reactions with permanganate and bromine, and had an nmr spectrum consistent with *sym*-bis(1,4-diphenyltriazol-5-yl)ethylene (XXVII) (singlet, 2 H, at τ 3.03, and aromatic multiplet, 20 H, centered at 2.4). Two bromine-containing products were obtained in much smaller amounts. One of them could be dehalogenated with zinc to give XXVII, and is therefore presumed to be the *sym*-dibromoethane derivative XXVIII. The second minor product could be obtained from XXVIII by dehydrohalogenation with alcoholic potassium hydroxide, and is therefore presumed to have structure XXIX. The stereochemistry is in every case unknown, although *trans* configurations can be presumed for the olefins on steric grounds.

When the position isomer of IV, 1,5-diphenyl-4-diazomethyl-1,2,3-triazole, XXX, was heated in benzene, cyclohexane, or cyclohexene, essentially the same result was obtained in each case (eq 12). The major product (64-66%) yield was always the corresponding aldazine, XXXI, accompanied by another substance, XXXII, resulting from loss of four nitrogen atoms from XXX (12-30% yield). An acetylenic function was



indicated by infrared absorption at 2100 cm^{-1} , formation of a copper salt with ammoniacal cuprous chloride, and reaction with bromine and with permanganate. Hydrolysis gave propiophenone and aniline, demonstrating that XXXII is the corresponding anil. No indication of carbenoid attack on the solvents was observed.

Discussion

It is easily recognized that the products of decomposition of 1,4-diphenyl-5-diazomethyl-1,2,3-triazole (IV) under the influence of either heat or light correspond to those of a carbene intermediate undergoing typical insertion or addition reactions, whereas the products from the position isomer, XXX, do not. Carbene formation as the rate-determining step in the reactions of IV is also indicated by the similarity of the rates of decomposition in benzene, cyclohexene, and cyclohexane, although the character of the product is different in each case. The behavior of IV is thus quite distinct from its nitrogen isostere, the azide I, which does not react with hydrocarbon solvents when decomposed in them, but instead gives a relatively inert primary decomposition product.

The isosteric substance derived from IV, which might be V or VI, is not formed as an isolable product. This suggests that V is much more reactive (as a carbene) than its nitrogen isostere, a circumstance that may reflect the lower stability to be expected of structures bearing a negative charge on carbon (Vb) compared to nitrogen (II), or that transformation to VI is less favored, owing to the higher energy of acetylenes (VI) compared to nitriles (III). Evidence has recently been presented that carboethoxycarbene is much more reactive than carboethoxynitrene, which may indicate a general relationship.⁹

Even when the possibility of intermolecular carbene reactions is denied, as in the decomposition of IV in hexafluorobenzene, no substance corresponding to V (or VI) could be detected; this observation suggests that V (or VI) is inherently unstable under even the mild conditions of the experiments. These considerations raise the interesting question of whether the acetylenic triazene structure (VI) might, when synthesized in an unambiguous manner, react as a triazolylcarbene in suitable media through equilibration with V.

The multiplicity of the carbene as it is initially formed from IV cannot, of course, be determined simply. With some diazoalkanes, evidence suggests that the singlet state is of higher energy and is formed first, subsequently decaying to a triplet ground state¹⁰ as a result of collisions. By virtue of the possibility of such limiting structures as Vb, however, the carbene derived from IV will very likely have a singlet ground state, which may or may not be formed through a triplet-state forerunner. It is therefore worthwhile to examine the behavior of IV for evidence bearing on this point.

Evidence of selectivity, as manifested in the ratio of addition to insertion in reaction with cyclohexene, is interesting but not conclusive. The ratios 7.7:1

(thermolysis at 60°) and 11.5:1 (photolysis at 10°) for diphenyltriazolylcarbene are probably not significantly different, in view of the large estimated error (10–20%) in their determination. It is, nevertheless, clear that diphenyltriazolyl carbene is markedly more selective than methylene, for which ratios of 1:1.54 and 1:2.13 have been determined. Even phenylcarbene¹¹ gives an addition–insertion ratio of only 1:1, and carboethoxycarbene¹² gives a ratio of about 2:1. Chlorocarbene and bromocarbene,¹³ on the other hand, show such high ratios that only the products of addition have been detected. The selectivity of diphenyltriazolylcarbene toward attack on cyclohexene and cyclohexane, $\sim 25:1$, may also be compared with that of the halocarbenes toward *cis*-2-butene and pentane, $>100:1$. Diphenyltriazolylcarbene thus falls between carboethoxycarbene and the halocarbenes in addition–insertion selectivity. The selectivity of diphenyltriazolylcarbene toward benzene (addition) and cyclohexane, 2.1:1, also places it qualitatively in the same position when compared to phenylcarbene,¹¹ which shows a ratio of 1.6:1.

The nature of the products from reaction with cyclohexene suggests that the foregoing carbenes, including diphenyltriazolylcarbene, react in the singlet state, for no products of hydrogen abstraction were observed. Diphenylcarbene, which is known to be a triplet in the ground state,¹⁴ converts cyclohexene in substantial amounts into bis(cyclohexenyl), becoming itself converted into tetraphenylethane, a reaction attributable to hydrogen abstraction by a triplet species and not paralleled by diphenyltriazolylcarbene.

Relative reactivity toward oxygen and carbon monoxide also suggests a singlet state for diphenyltriazolylcarbene. Both triplet methylene and diphenylcarbene react readily with molecular oxygen,¹⁵ whereas diphenyltriazolylcarbene reacts only to a very minor extent. Singlet methylene, on the other hand, reacts readily with carbon monoxide,¹⁶ to give ketene and its transformation products, as diphenyltriazolylcarbene also appears to do (it is unfortunate that we were unable to characterize the products more satisfactorily, and thus to establish the point firmly, but the over-all reactions form an involved sequence leading to complex products).

In addition to the foregoing similarities of the carbene derived from IV to those derived from other diazo compounds, IV has the notable characteristic of being an unusually clean carbene source. The facts that it gives rise to carbene-derived products in high yield and requires neither light nor catalyst to do so provide obvious opportunities for studying carbene reactions unobscured by the ambiguities engendered by photoexcitation or the possibility of complex formation with heavy metals.

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(13) G. L. Closs and J. J. Coyle, *J. Amer. Chem. Soc.*, **87**, 4270 (1965).

(14) R. M. Etter, H. S. Skovronek, and P. S. Skell, *ibid.*, **81**, 1008 (1959).

(15) W. Kirmse, L. Horner, and H. Hoffman, *Ann.*, **614**, 19 (1958); R. F. W. Bader and J. I. Generosa, *Can. J. Chem.*, **43**, 163 (1965).

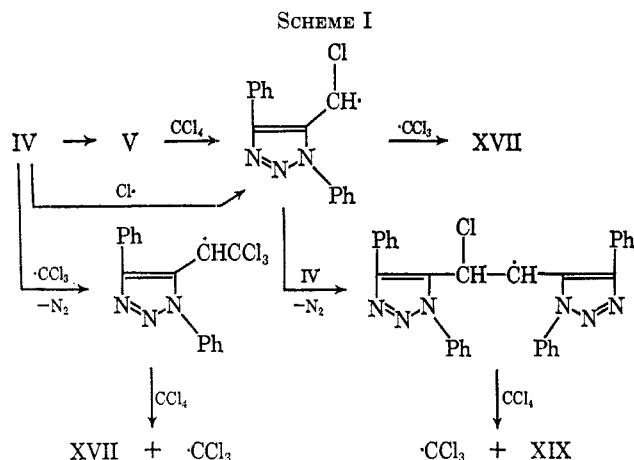
(16) H. M. Frey, in "Carbene Chemistry," W. Kirmse, Ed., Academic Press Inc., New York, N. Y., 1964, pp 217–233.

(9) J. E. Baldwin and R. A. Smith, *J. Amer. Chem. Soc.*, **89**, 1886 (1967).

(10) E.g., E. Wasserman, L. Barash, and W. A. Yager, *ibid.*, **87**, 2075 (1965) (cyanomethylene and dicyanomethylene).

The decomposition of IV in carbon tetrachloride solution is clearly a different type of process from that in the other solvents studied. The rate is an order of magnitude greater, and the reaction has autocatalytic features. Furthermore, the products are those to be expected of a free-radical process, a possibility for which is shown in Scheme I (the hexachloroethane observed could arise from the trichloromethyl radicals formed).

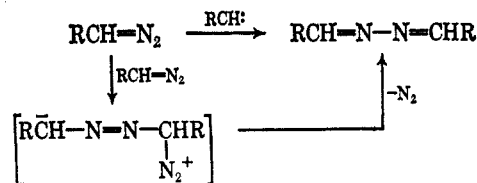
Similar behavior has been reported for the decomposition of diphenyldiazomethane in bromotrichloromethane,¹⁷ of methyl diazoacetate in chloroform,¹⁷ and of diazomethane in carbon tetrachloride.¹⁷



It is interesting that IV apparently does not cyclize by insertion of the intermediate carbene at one of the *ortho* positions of the adjacent phenyl groups, for *o*-diazomethylbiphenyl, which is structurally very similar, gives high yields of fluorene when decomposed. We believe this to be a steric effect applying to cyclization of 5-substituted 1,4-diaryltriazoles in general, for we were unable to accomplish cyclodehydration of the corresponding carboxylic acid with either polyphosphoric acid or hydrogen fluoride, even though such treatment converts *o*-phenylbenzoic acid into fluorenone. Other examples of vicinal phenyltriazolecarboxylic acids have also been reported to resist cyclization.¹⁸

It is also of interest that the carbene from IV does not dimerize to an olefin, for such a reaction has been observed with a number of sterically hindered diazoalkanes.¹⁹ Presumably the explanation lies in the fact that V reacts very rapidly with the solvent in which it is generated.

The position isomer of IV, XXX, does not give rise to the insertion and addition products to be expected from a carbene intermediate. Although the formation of aldazine from a diazoalkane, the major reaction in this case, has been attributed to a carbene reacting with undecomposed diazoalkane,²⁰ there is good evidence that aldazines may be formed by direct dimerization of diazoalkane with loss of nitrogen;²¹ the latter path may obtain with XXX.



The second product, the anil of phenyl ethynyl ketone (XXXII), may have arisen from a carbene if the loss of a second molecule of nitrogen (from the triazole ring) is faster than bimolecular reactions of the carbene, but such a situation is not distinguishable from concerted loss of two molecules of nitrogen. On the other hand, it should be noted that there are also marked reactivity differences between the 1,4-diphenyltriazole and 1,5-diphenyltriazole systems that do not involve loss of nitrogen; *e.g.*, the formation of the hydrazones from the aldehydes, the oxidation of the aldehyde hydrazones, the thermal stability of the diazomethyl derivatives, and the base-catalyzed deformylation of the aldehydes. It cannot be said at this time if there is a close relationship between such differences and the formation of carbene intermediates.

Although the yields of acetylenic anil were low, this reaction may have some synthetic interest, for there does not appear to be a feasible alternative route to such a structure (the reaction of aniline with the corresponding ketone gives instead a different type of product, resulting from addition of aniline across the triple bond).

Experimental Section

1,4-Diphenyl-5-cyano-1,2,3-triazole (XII). A. From 1,4-Diphenyl-5-chloro-1,2,3-triazole (XI).²²—A mixture of 2.00 g (0.00785 mol) of XI²² with a well-stirred suspension of sodium cyanide (1.47 g) in 25 ml of dimethyl sulfoxide was heated at 140° for 4 hr, whereupon the mixture was poured into cold water and extracted with ether. Drying of the ethereal extract over anhydrous sodium sulfate followed by removal of the ether under reduced pressure gave a white crystalline solid, which was recrystallized from absolute ethanol to give 1.47 g (75%) of the nitrile XII, mp 121–124°. The infrared spectrum showed absorptions at 2260, 1600, 1500, 1080 and 1000 (doublet) cm⁻¹. An analytical sample prepared by three recrystallizations from ethanol-petroleum ether (bp 60–75°) had mp 122–123°. Extending the reaction time to 12 hr resulted in a much lower yield.

Anal. Calcd for C₁₅H₁₀N₄: C, 73.15; H, 4.10. Found: C, 73.06; H, 4.20.

B. From 1,4-Diphenyl-1,2,3-triazole-5-carboxaldehyde Oxime.²⁴—A solution of 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde oxime (0.50 g, 0.00189 mol) in 10 ml of freshly distilled acetic anhydride was heated under a short Vigreux column so that acetic acid slowly distilled. After 1 hr excess acetic anhydride was removed under reduced pressure leaving a white crystalline solid. Recrystallization from absolute ethanol gave 0.38 g of XII (81%), mp 122–123.5°.

1,4-Diphenyl-1,2,3-triazole-5-carboxaldehyde (VII).²⁵—A 2.0-g portion of Raney nickel alloy was stirred for 30 min with 2 N sodium hydroxide. The liquid was then decanted and the nickel washed twice with water. A solution of 1.00 g (0.0041 mol) of XII in 75 ml of 90% formic acid was added to the nickel, the suspension was heated to 75°, and 50 ml of absolute ethanol was added. The hot solution was filtered and concentrated to

(17) (a) A. R. M. Murray and A. M. Trozzolo, *J. Org. Chem.*, **27**, 3341 (1962); (b) W. H. Urry and J. W. Wilt, *J. Amer. Chem. Soc.*, **76**, 2594 (1954); (c) W. H. Urry and J. R. Eisner, *ibid.*, **73**, 2977 (1951); **74**, 5822 (1952).

(18) W. Borsche, H. Hahn, and M. Wagner-Roemmick, *Ann.*, **554**, 15 (1943).

(19) H. E. Zimmerman and D. H. Paskovich, *J. Amer. Chem. Soc.*, **86**, 2149 (1964).

(20) H. Reimlinger, *Chem. Ber.*, **97**, 339 (1964).

(21) C. G. Overberger and J. P. Anselme, *J. Org. Chem.*, **29**, 1188 (1964); P. Yates, D. G. Farnum, and D. W. Wiley, *Tetrahedron*, **18**, 881 (1962).

(22) L. Friedman and H. Shechter, *J. Org. Chem.*, **26**, 877 (1960).

(23) H. W. Carnelly and P. V. Dutt, *J. Chem. Soc.*, **125**, 2476 (1924).

(24) Following the general method given by A. I. Vogel ("Practical Organic Chemistry," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1962, p 804).

(25) B. Staskun and O. G. Backeberg, *J. Chem. Soc.*, 5880 (1965).

half the original volume, and water was added to the cloud point. On cooling, 0.46 g (56%) of VII, mp 169–170°, crystallized. It was identical (mixture melting point, infrared spectrum, R_f value) with a sample prepared by the method of Sheehan and Robinson.⁴

1,4-Diphenyl-1,2,3-triazole-5-carboxaldehyde Tosylhydrazone.²⁶—A solution of 5.0 g (0.002 mol) of VII and 3.7 g (0.002 mol) of *p*-toluenesulfonylhydrazine in 200 ml of methanol was heated under reflux for 3 hr. The hot solution was filtered to remove traces of the corresponding aldazine²⁷ and then allowed to cool. The tosylhydrazone crystallized in long white needles, mp 125° with rapid evolution of gas, and weighed 7.7 g (92%). An analytical sample prepared by recrystallization from benzene-petroleum ether mixture below room temperature had mp 128–130°.

Anal. Calcd for $C_{22}H_{19}N_5O_2S$: C, 63.29; H, 4.59. Found: C, 63.48; H, 4.74.

1,5-Diphenyl-1,2,3-triazole-4-carboxaldehyde Tosylhydrazone.—This substance was prepared in the foregoing manner in 95% yield; after recrystallization from chloroform-petroleum ether and benzene-petroleum ether mixtures, it had mp 175–177° with gas evolution.

Anal. Calcd for $C_{22}H_{19}N_5O_2S$: C, 63.29; H, 4.59. Found: C, 62.91; H, 4.66.

1,4-Diphenyl-5-diazomethyl-1,2,3-triazole (IV).²⁸—1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde tosylhydrazone (3.0 g, 0.0072 mol) was partially dissolved in 200 ml of anhydrous ether in a carefully dried apparatus, and cooled to –50°. The system was filled with dry nitrogen and protected from moisture while 6.0 ml of a 1.5 *N* solution of butyllithium in pentane was added dropwise by means of a syringe. The reaction mixture was then allowed to warm slowly to 20°, stirred for 24 hr at that temperature, and filtered. Concentration to a small volume in a stream of nitrogen and cooling in a Dry Ice-acetone bath gave 1.04 g (55%) of bright orange crystals which were sufficiently pure for most purposes, mp 110° with rapid gas evolution. The infrared spectrum showed an intense absorption at 2060 cm^{-1} and other maxima at 1600, 1560, 1500, 1080 and 1000 cm^{-1} . The nmr spectrum showed a singlet at τ 5.2 and a multiplet centered at 2.7 (area ratio 1:10). The ultraviolet spectrum in methanol showed λ_{max} 240 $m\mu$ ($\log \epsilon$ 4.35) with a shoulder at 282 $m\mu$, and λ_{max} 462 $m\mu$ ($\log \epsilon$ 1.75). An analytical sample was prepared by three recrystallizations from ether-petroleum ether mixture between room temperature and that of a Dry Ice-acetone bath; the melting-decomposition point was unchanged.

Anal. Calcd for $C_{15}H_{11}N_5$: C, 68.94; H, 4.25; N, 26.81. Found: C, 68.85; H, 4.19; N, 26.74.

Treatment of the diazoalkane with bromine gave a single product identical with 1,4-diphenyl-5-dibromomethyl-1,2,3-triazole prepared from 1,4-diphenyl-5-methyl-1,2,3-triazole (see ahead).

1,4-Diphenyl-1,2,3-triazole-5-carboxaldehyde Hydrazone (VIII).—A solution of 1.00 g (0.004 mol) of VII and 1.33 g (0.042 mol) of anhydrous hydrazine²⁹ in 50 ml of absolute ethanol was heated under reflux for 4 hr and allowed to cool. A 0.140-g sample of a pale green, insoluble solid (the azine, IX), mp 300–305°, was filtered off, and the mother liquor was diluted with water and extracted with benzene. The benzene extract was dried over anhydrous sodium sulfate, concentrated to a small volume and chromatographed on 50 g of Florisil. Elution with 1% ether in benzene gave 0.035 g (4%) of 1,4-diphenyl-1,2,3-triazole, mp 179–182°. Elution with 2% ether in benzene gave 0.480 g (45%) of a white, somewhat oily, solid (VIII), mp 92–99°. Elution with 5% ether in benzene gave an additional 0.053 g of IX (total yield 19%).

The infrared spectrum of crude VIII had absorptions at 3410, 3310, and 3220 cm^{-1} (N–H), weak absorption at 1640 (C=N), and absorptions at 1600, 1500 and 1080, and 1000 cm^{-1} , indicating the presence of phenyl and 1,2,3-triazole rings. The nmr spectrum contained a broad singlet at τ 4.22 and a complex multiplet centered at 2.5 (relative areas approximately 1:6).

An analytical sample prepared by three recrystallizations from ethanol-petroleum ether had mp 106–108°.

Anal. Calcd for $C_{15}H_{11}N_5$: C, 68.42; H, 4.97. Found: C, 68.75; H, 4.64.

Structural assignment was confirmed by oxidation with mercuric oxide to 1,4-diphenyl-5-diazomethyl-1,2,3-triazole (IV).

The infrared spectrum of IX showed C=N absorption at 1625 and other absorptions at 1590, 1550, 1500, 1070, and 990 cm^{-1} (phenyl and 1,2,3-triazole rings); N–H absorption was lacking. The nmr spectrum of IX in trifluoroacetic acid exhibited a singlet at τ 1.63 and an unresolved multiplet centered at 2.2 (relative areas 1:10). An analytical sample, prepared by three recrystallizations each from dimethylformamide and dimethylformamide-*p*-xylene mixture, had mp 302–303°. This substance, the azine of VII, was also prepared in quantitative yield by heating an ethanol solution of 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde and its hydrazone for 3 hr.

Anal. Calcd for $C_{15}H_{11}N_4$: C, 72.85; H, 4.49; N, 22.66. Found: C, 73.04; H, 4.33; N, 22.80.

When a large excess of hydrazine (100-fold) was employed to suppress azine formation from the aldehyde, a quantitative yield of the deformylation product, 1,4-diphenyl-1,2,3-triazole (X), was obtained instead.

Deformylation of 1,4-Diphenyl-1,2,3-triazole-5-carboxaldehyde (VII) with Sodium Methoxide.—A solution of 0.23 g of freshly cut metallic sodium and 1.00 g (0.004 mol) of VII in 50 ml of anhydrous methanol was refluxed for 12 hr in a vessel provided with a Dry Ice condenser, after which time 25 to 30 ml of liquid was distilled into a receiver containing 0.435 g of phenylhydrazine. The distillate was then refluxed for 8 hr, after which the methanol was evaporated. The oily residue readily crystallized to give 0.080 g of a white solid, mp 136–140°, identical with an authentic sample of *N*'-phenylformylhydrazide prepared from ethyl formate and phenylhydrazine under the same conditions in 15% yield. (If it can be assumed that the yield of hydrazide is the same in both instances, 98% of the theoretical amount of ethyl formate is accounted for.) On cooling the solution remaining in the original reaction vessel, 0.83 g (93%) of 1,4-diphenyl-1,2,3-triazole (X) was obtained.

Under the same reaction conditions, the position isomer, 1,5-diphenyl-1,2,3-triazole-4-carboxaldehyde, was recovered quantitatively.

1,5-Diphenyl-1,2,3-triazole-4-carboxaldehyde Hydrazone.—A solution of 5.0 g (0.02 mol) of 1,5-diphenyl-1,2,3-triazole-4-carboxaldehyde and 5.6 g of 95% hydrazine in 50 ml of absolute ethanol was refluxed for 1 hr and then concentrated to one-half its original volume; water was added to the cloud point. The hydrazone separated on cooling, and was recrystallized from benzene-petroleum ether mixture; it weighed 6.9 g (78%) and had mp 150–152° (unchanged by four recrystallizations from benzene-petroleum ether mixture). The infrared spectrum lacked carbonyl absorption but exhibited maxima at 3450, 1600, 1500, and 1080 and 1000 (doublet) cm^{-1} . The nmr spectrum showed singlets at τ 2.60 and 4.67 (broad) and a multiplet centered at 3.1 (relative areas 1:2:10).

Anal. Calcd for $C_{15}H_{11}N_5$: C, 68.42; H, 4.97. Found: C, 68.40; H, 5.09.

1,5-Diphenyl-4-diazomethyl-1,2,3-triazole (XXX).—A suspension of 5.00 g (0.019 mol) of 1,5-diphenyl-1,2,3-triazole-4-carboxaldehyde hydrazone, 16.5 g of active manganese dioxide,⁵ and 20 g of anhydrous sodium sulfate in 500 ml of anhydrous ether was stirred for 15 min in the dark. A 5-ml portion of saturated alcoholic potassium hydroxide was added and stirring was continued for 5 hr at room temperature. The reaction mixture was filtered and the filtrate evaporated to one-half its original volume in a stream of nitrogen. Petroleum ether was added to the cloud point and the solution refrigerated overnight. A small amount of white solid was filtered off, the solution was concentrated, petroleum ether was added, and the flask was returned to the refrigerator for 24 hr. Repetition of this process gave three crops of orange-red crystals having a combined weight of 2.39 g (48%), mp 110° with rapid evolution of gas (unchanged by three recrystallizations from ether-petroleum ether mixture). The infrared spectrum lacked NH absorption and showed an intense maximum at 2080 cm^{-1} (C=N₂) as well as maxima at 1080 and 100 cm^{-1} (characteristic of 1,2,3-triazoles³⁰). The

(26) General method of G. L. Closs, L. E. Closs, and W. A. Boll [*J. Amer. Chem. Soc.*, **85**, 3796 (1963)].

(27) Cf. F. C. Chang, *J. Org. Chem.*, **30**, 2053 (1965), for another example of azine formation during the preparation of a tosylhydrazone.

(28) Based on the general method of G. W. Kaufman, J. A. Smith, C. G. Vander Stouw, and H. Shechter, *J. Amer. Chem. Soc.*, **87**, 935 (1965).

(29) L. I. Smith and K. L. Howard, *Org. Syn.*, **24**, 53 (1944).

(30) J. H. Boyer in "Heterocyclic Compounds," Vol. 7, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, pp 384–361.

nmr spectrum showed a singlet at τ 5.28 and a complex multiplet centered at 3.1 with relative areas of 1:10.

Anal. Calcd for $C_{15}H_{11}N_5$: C, 68.95; H, 4.24. Found: C, 68.83; H, 4.16.

1,4-Diphenyl-5-hydroxymethyl-1,2,3-triazole.—A solution of 1.0 g (0.004 mol) of VII and 1.5 g of sodium borohydride in 50 ml of methanol was allowed to stand overnight, and was then heated on a steam bath for a few minutes and diluted with 100 ml of 2% hydrochloric acid. The white solid that formed on cooling was recrystallized from an ethanol-water mixture to give 0.78 g of the alcohol, mp 169–170.5° (unchanged by three recrystallizations each from aqueous ethanol and benzene-petroleum ether mixture). Its infrared spectrum showed absorptions at 3320, 1600, 1500, 1260, 1080, 1025, and 1000 cm^{-1} and lacked carbonyl absorption. The nmr spectrum showed singlets at τ 5.25 and 6.90 and a multiplet centered at 2.5; relative areas were 2:1:10.

Anal. Calcd for $C_{15}H_{13}N_3O$: C, 71.70; H, 5.22; N, 16.72. Found: C, 71.88; H, 5.20; N, 16.82.

1,4-Diphenyl-5-chloromethyl-1,2,3-triazole (XXII).—A solution of 7.0 g (0.0278 mol) of 1,4-diphenyl-5-hydroxymethyl-1,2,3-triazole in 20 ml of thionyl chloride was allowed to stand for 4 hr at room temperature, and thereupon heated for 1 hr on the steam bath. Excess thionyl chloride was removed under reduced pressure, leaving an oil, which crystallized on scratching. Recrystallization from petroleum ether-benzene gave 5.6 g (75%) of the chloromethyl compound, mp 115–117°. Its infrared spectrum lacked -OH absorption and exhibited maxima at 1600, 1500, and 1080, and 1000 cm^{-1} (phenyl and 1,2,3-triazole rings). The nmr spectrum showed a singlet at τ 5.40 and a multiplet centered at 2.4 (area ratio 1:5). An analytical sample, prepared by three recrystallizations from benzene-petroleum ether, had mp 116–117°.

Anal. Calcd for $C_{15}H_{12}N_3Cl$: C, 66.79; H, 4.48; N, 15.58. Found: C, 66.87; H, 4.56; N, 15.44.

1,4-Diphenyl-5-methyl-1,2,3-triazole.³¹—A solution of 5.00 g (0.0372 mol) of phenylacetone, 5.44 g (0.0456 mol) of phenyl azide, and 2.72 g of sodium methoxide in 100 ml of absolute ethanol was heated under reflux for 4 hr. On cooling, a white solid crystallized. Recrystallization from ethanol gave 6.0 g (69%) of product, mp 157–159°. The infrared spectrum showed absorptions at 1600, 1500, 1080, and 1000 cm^{-1} (phenyl and 1,2,3-triazole rings); the nmr spectrum showed a singlet at τ 7.60 (Ar-CH₃) and a complex multiplet centered at 2.5, area ratios 3:10. These data are in good accord with 1,4-diphenyl-5-methyl-1,2,3-triazole. An analytical sample prepared by four recrystallizations from ethanol-petroleum ether had mp 158–159°.

Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; mol wt, 235. Found: C, 76.15; H, 5.69; mol wt (cryoscopic in benzene), 244.

1,4-Diphenyl-5-dibromomethyl-1,2,3-triazole (XXVI).—A solution of 5.25 g (0.0223 mol) of 1,4-diphenyl-5-methyl-1,2,3-triazole, 8.76 g (0.0491 mol) of N-bromosuccinimide and 1.00 g of benzoyl peroxide in 400 ml of carbon tetrachloride was heated under reflux for 24 hr. The solution was filtered hot, washed several times with water, dried over anhydrous sodium sulfate, concentrated, and chromatographed on 250 g of silica gel. The main product (XXVI) was eluted from the column with 1% ether in benzene (following a small band of yellow oil) to yield 5.17 g (70%): mp 144–146°; infrared absorptions at 1600, 1500, 1080, and 1000 cm^{-1} (phenyl and 1,2,3-triazole rings); nmr, singlet at τ 3.25 (Ar-CH) and a multiplet centered at 2.3, relative areas 1:10. An analytical sample prepared by four recrystallizations from carbon tetrachloride-petroleum ether mixture had mp 145–146°.

Anal. Calcd for $C_{15}H_{11}N_3Br_2$: C, 45.83; H, 2.82. Found: C, 45.86; H, 2.78.

The foregoing product was identical with a sample obtained by treating the aldehyde (VII) with phosphorus pentabromide in refluxing methylene chloride (yield 85%).

A sample of XXVI was heated for 3 hr with alcoholic potassium hydroxide; 1,4-diphenyl-1,2,3-triazole (X) was produced essentially quantitatively. A similar experiment conducted at room temperature overnight led to a mixture of X and aldehyde VII.

Thermolysis of 1,4-Diphenyl-5-diazomethyl-1,2,3-triazole (IV). **A. In Benzene.**—A solution of 0.279 g (0.0011 mol) of IV in 75 ml of anhydrous benzene was heated at 50° under

nitrogen for 4 hr, after which time the orange color had completely disappeared. A pale green, insoluble solid, 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde azine (IX), mp 300–304°, wt 0.020 g (8%), was separated by filtration. Thin layer chromatography of the mother liquor showed a single product. Chromatography on 75 g of alumina gave 0.220 g (66%) of XIV as colorless crystals, mp 162–166° (eluted with 75% ether in petroleum ether). Compound XIV decolorized both bromine and potassium permanganate, and showed infrared absorptions at 1600, 1500, 1080, and 1000 cm^{-1} (phenyl and 1,2,3-triazole rings and nmr signals at τ 6.87 (triplet), 4.68 (quartet), 3.77 (multiplet), 3.40 (multiplet), and 2.5 (complex multiplet)). An analytical sample prepared by two recrystallizations each from benzene-petroleum ether had mp 167–167.5°.

Anal. Calcd for $C_{21}H_{17}N_5$: C, 81.00; H, 5.51; N, 13.50. Found: C, 80.81; H, 5.70; N, 13.42.

On heating XIV under reflux with maleic anhydride in xylene for 0.5 hr, an adduct, mp 257° with decomposition, was obtained, confirming the presence of a conjugated olefin.³²

Anal. Calcd for $C_{25}H_{19}N_5O_3$: C, 73.34; H, 4.68; N, 10.26. Found: C, 73.41; H, 4.46; N, 10.01.

A reaction carried out in more dilute solution (0.005 M) differed only in that no azine was formed. When oxygen was bubbled through a 0.005 M benzene solution of diazoalkane heated at 50° for 4 hr, a low yield (3%) of 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde (VII), isolated as the 2,4-dinitrophenylhydrazone, was obtained as well. No aldehyde was produced in the absence of oxygen. In a similar experiment using carbon monoxide in place of oxygen, an oily solid remained after evaporation of the excess benzene. No acidic substance could be extracted with base, and no pure substance could be separated. Strong infrared absorptions at 1740 and 1660 cm^{-1} showed that much reaction with the carbon monoxide must have taken place. The nmr spectrum showed peaks characteristic of the cycloheptatriene system, and many other peaks having nonintegral area ratios. Compound XIV was stable under these reaction conditions.

B. In Cyclohexane.—A solution of 0.135 g (0.52 mmol) of IV in 35 ml of freshly redistilled cyclohexane was placed in a flask connected to a gas buret, and the system was flushed with dry nitrogen. The solution was heated with stirring for 24 hr at 40°; 0.54 mmol of nitrogen was evolved. A pale green precipitate of aldazine IX (0.018 g, 14%) was removed by filtration. Thin layer chromatography revealed only a single product in the mother liquor. Vapor phase chromatography failed to show any traces of bicyclohexyl. Removal of cyclohexane left an oily yellow solid, from which 0.110 g (67%) of a white solid (XV) was obtained by recrystallization from aqueous ethanol: mp 126–131°; infrared absorptions at 1600, 1500, 1070, and 995 cm^{-1} (phenyl and 1,2,3-triazole rings); and nmr signals at τ 8.6 (multiplet), 9.1 (multiplet) 7.25 (doublet), and 2.5 (complex multiplet), with relative areas approximately 11:2:10. An analytical sample prepared by three recrystallizations from petroleum ether had mp 132.5–134.0°.

Anal. Calcd for $C_{21}H_{23}N_3$: C, 79.46; H, 7.30; N, 13.24. Found: C, 79.65; H, 7.17; N, 13.25.

C. In Cyclohexene.—A solution of 0.500 g (0.0019 mol) of IV in 38 ml of freshly redistilled cyclohexene was heated for 4 hr at 50° under dry nitrogen. Thin layer chromatography showed a single, elongated spot with an R_f value approximately the same as for 1,4-diphenyl-5-cyclohexylmethyl-1,2,3-triazole (XV). No 2,2-bicyclohexenyl could be detected by vapor phase chromatography. Cyclohexene was removed *in vacuo*, and the residue was dissolved in ethanol and hydrogenated at room temperature and 35 psi for 3 hr over a platinum catalyst. Chromatography on 80 g of silica gel partially separated the reaction mixture into two components: XVI, mp 143–151°, and a compound, mp 127–132°, identical with XV. A total of 0.466 g of XVI and XV combined were eluted from the column with 2% ether in benzene. Compound XVI was stable to hydrogenation and reacted sluggishly with bromine and not at all with potassium permanganate. Its infrared spectrum had absorptions at 1600, 1500, 1080, and 1000 cm^{-1} . The nmr spectrum had incompletely resolved multiplets at τ 8.0, 8.4, 8.8, and 9.3 and a complex multiplet centered at 2.5 (aliphatic H-aromatic H approximately 11:10). Resonances corresponding to olefinic, allylic, or benzylic protons were completely absent. These data

(31) General method of O. Dimroth, E. Fusoni, and S. Marshall, *Ber.*, **39**, 3920 (1906).

(32) K. Alder, H. Jungen, and K. Rust, *Ann.*, **602**, 94 (1957); N. W. Gordon and I. W. Elliott, *J. Org. Chem.*, **27**, 1445 (1962).

are consistent with 7-(1,4-diphenyl-1,2,3-triazole-5-yl)norcarane. Compound XVI was also obtained by hydrogenation of 7-(1,4-diphenyl-1,2,3-triazole-5-yl) cycloheptatriene (XIV) with a platinum catalyst. An analytical sample prepared by three recrystallizations each from aqueous ethanol and petroleum ether had mp 150–153°.

Anal. Calcd for $C_{21}H_{21}N_3$: C, 79.97; H, 6.72; N, 13.32. Found: C, 79.97; H, 6.71; N, 12.95.

A ratio of 7.7:1 for XV–XVI was determined from the nmr spectrum of the reaction mixture after hydrogenation by comparing the normalized area of the methylene doublet of XV at τ 7.25 with that of remaining aliphatic protons in the region 7.7–9.8. A correction for the contribution of the aliphatic protons of XV estimated from the methylene doublet at τ 7.25, was applied to this latter area. Similar ratios of addition to insertion were obtained by recombining chromatographic fractions containing XVI, XV, and mixtures thereof and from the nmr spectrum of the reaction mixture before hydrogenation. Since the combined yield of XVI and XV was 0.466 g, this ratio corresponds to 0.412 g (69%) of XVI and 0.054 g ($9 \pm 3\%$) of XV. The error was estimated by adding a known amount of XV to the mixture and comparing calculated and observed increases in the area of the methylene doublet at τ 7.25.

D. In Carbon Tetrachloride.—A solution of 0.804 g (0.003 mol) of IV in 150 ml of freshly redistilled and deoxygenated carbon tetrachloride was heated under nitrogen for 4 hr at 50°, at which time it had become colorless. The solution was concentrated and examined by vapor phase chromatography, which revealed small amounts of hexachloroethane. Column chromatography on 30 g of Florisil gave 0.505 g (42%) of a white crystalline solid, XVII, mp 132–137°, eluted with 1% ether in benzene. Elution with 10% ether in benzene gave 0.467 g of a second compound, XIX, mp 260° with extensive decomposition. The experiment was repeated several times and varying amounts of aldehyde (XII) were occasionally isolated; careful purification of the diazoalkane eliminated it. Three further potential sources of XII were also eliminated. When oxygen was bubbled through a carbon tetrachloride solution of pure diazoalkane for 4 hr at 50°, no detectable amount of aldehyde was formed, and 1,4-diphenyl-5-dichloromethyl-1,2,3-triazole mp 131–134°, prepared from XII and phosphorus pentachloride, underwent no hydrolysis under the experimental conditions. Compound XVII was also found to be stable under the experimental conditions.

Compound XVII gave a positive test for halogen (sodium fusion). Its infrared spectrum showed absorptions at 1600, 1500, 1080, and 1000 cm^{-1} . The nmr spectrum showed a singlet at τ 4.22 and a multiplet centered at 2.5, relative areas 1:10. Recrystallization from isopropyl alcohol gave an analytical sample, mp 143–143.5°.

Anal. Calcd for $C_{16}H_{11}Cl_2N_3$: C, 49.64; H, 2.87; N, 10.86. Found: C, 49.71; H, 2.95; N, 11.04.

When XVII was heated in an alcoholic potassium hydroxide solution for 0.5 hr, a white, crystalline, chlorine-containing compound, mp 221–223°, precipitated. Its infrared spectrum showed absorption at 1625 ($\text{C}=\text{C}$ stretching) and at 1600, 1500, 1080, and 1000 cm^{-1} (phenyl and 1,2,3-triazole rings). The nmr spectrum showed only aromatic protons (multiplet centered at τ 2.4). These data are consistent with 1,4-diphenyl-5-trichlorovinyl-1,2,3-triazole (XIX). An analytical sample prepared by two recrystallizations each from ethanol–water and benzene–petroleum ether had mp 221–222°.

Anal. Calcd for $C_{16}H_{10}N_3Cl_3$: C, 54.81; H, 2.88; N, 11.99. Found: C, 55.20; H, 2.95; N, 11.98.

Compound XIX contained halogen, and its infrared spectrum showed absorptions at 1600, 1510, 1080, and 1000 cm^{-1} . It was found to be identical with the 1,2-dichloro-1,2-bis(1,4-diphenyltriazol-5-yl)ethane prepared by addition of chlorine to 1,2-bis(1,4-diphenyltriazol-5-yl)ethylene (XXI) (see below).

When XIX was dissolved in hot acetic acid and heated in the presence of zinc dust for 4 hr, 1,2-bis(1,4-diphenyl-1,2,3-triazol-5-yl)ethylene (XXXI) was produced in good yield. A chloroform solution of XXI (prepared from 1,4-diphenyl-5-dibromomethyltriazole; see ahead) was saturated with chlorine and allowed to stand overnight at room temperature; 1,2-dichloro-1,2-bis(1,4-diphenyltriazol-5-yl)ethane, mp 225–256° with extensive decomposition, identical with XIX, was obtained in 50% yield. In a later experiment, XIX was isolated in a pure state in a yield of 45%, mp 270° with extensive decomposition.

Anal. Calcd for $C_{30}H_{22}N_6Cl_2$: C, 67.04; H, 4.13; N, 15.64. Found: C, 67.32; H, 4.21; N, 15.34.

E. Without Solvent or in the Presence of Inert Diluent.—A suspension of IV in perfluorodioxane (Minnesota Mining and Manufacturing Co. FC-75) heated for 24 hr at 60° yielded only the azine (IX) (76% yield).

A solution of IV in hexafluorobenzene evolved gas when heated, but evaporation of the solvent left a tarry residue from which no pure substance could be isolated; it was free of fluorine.

Thermal decomposition of IV under nitrogen without any solvent led to mild explosions, and left tarry residues from which the only identifiable material obtained was small amounts of the aldazine (IX).

Photolysis of IV.—Experiments were carried out in a thin-walled Pyrex tube with a quartz water jacket. Coolant water was precirculated through a copper coil immersed in an ice–salt bath. An external light source was provided by a Srinivasan-Rayonet-Griffin Photochemical Reactor (Southern New England Ultra-violet Co.) equipped with 16 0.24-W RPR-3500-Å lamps emitting 90% of their energy in the 3500-Å region.

A. In Benzene.—A solution of 0.500 g (0.0019 mol) of IV in 75 ml of anhydrous benzene was photolyzed for 24 hr at 10°, during which time the orange color of the diazoalkane disappeared. In the absence of light, 98% of the diazoalkane remained unreacted under these conditions. Thin layer chromatography revealed a single product. Removal of benzene gave a crystalline residue, which on recrystallization yielded 0.411 g (69%) of 7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (XIV), mp 159–164°, identical with that obtained from the thermal reaction (mixture melting point after recrystallization).

When the photolysis was conducted while oxygen was bubbled through the solution, no 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde was produced in detectable amounts (infrared; di-nitrophenylhydrazones precipitation).

B. In Cyclohexane.—A solution of 0.350 g (0.0013 mol) of IV in 60 ml of freshly redistilled cyclohexane was photolyzed 30 hr at 10°. In the absence of light, 95% of the diazoalkane was unreacted under these conditions. Thin layer chromatography showed a single elongated spot with an R_f value identical with that found in the thermal reaction. Vapor-phase chromatography failed to show any traces of 2,2'-bicyclohexenyl. Chromatography on 50 g of Florisil and elution with 2% ether in benzene partially separated the reaction mixture into two components, 7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcarane (XVI) and 1,4-diphenyl-5-cyclohexylmethyl-1,2,3-triazole (XV). The addition–insertion ratio was determined from the nmr spectrum to be 11.5:1. The combined yield of 0.263 g corresponds to 0.242 g (57%) of the norcarane and 0.021 g ($5 \pm 3\%$) of the cyclohexylmethyltriazole (XV).

Competitive Reactions with Hydrocarbons. A. With Benzene and Cyclohexane.—A solution of 0.300 g (0.00115 mol) of IV in 100 ml of an equimolar mixture of benzene and cyclohexane was heated under nitrogen for 4 hr at 60°. Solvents were removed under reduced pressure, and the residue was redissolved in chloroform. By comparison of the normalized areas of the nmr triplet of XIV at τ 6.87 and the methylene doublet of XV at 7.25, the ratio of XIV–XV was found to be 2.1:1. Chromatography of the reaction mixture on 30 g of Florisil gave 0.311 g of a mixture of XIV and XV, mp 125–155°, eluted with 20% petroleum ether–benzene, and 0.36 g (13%) of the azine (IX), mp 300–305°, eluted with 1:1 ether–benzene. The mixture of XIV and XV was heated 20 min with 0.084 g of maleic anhydride in xylene solution. The solid adduct was filtered from the cooled mixture, the xylene was evaporated from the filtrate, the residue was taken up in hot carbon tetrachloride and filtered from a further small amount of solid. Evaporation left 0.110 g of XV, mp 130–134° (mmp 132–134°). The molar ratio of XIV–XV was therefore 2.05:1. A duplicate experiment using chromatography on silica gel gave 0.264 g of the XIV–XV mixture, from which thorough washing with petroleum ether extracted 0.086 g of XV, mp 125–130°, and left 0.180 g of XIV: molar ratio of XIV–XV = 2.15:1.

B. With Benzene and Cyclohexane.—In a similar experiment using an equimolar mixture of benzene and cyclohexane, relative amounts of XVI and XIV were determined by comparison of the normalized areas of the olefinic protons of XIV at τ 3.40, 3.77, and 4.68 with that of the aliphatic protons of XVI in the region 7.5–9.6. The olefinic protons of XIV at τ 3.40 and 3.77 were clearly resolved, but those at 4.68 were partially obscured by small amounts of insertion products from the diazoalkane and cyclohexene, causing the combined area of these three groups to be somewhat large, and thus to give only a minimum value for

the ratio of XVI-XIV. A maximum value was obtained by selecting the smallest area from the three groups. The most accurate value of the XVI-XIV ratio, obtained from the cleanly resolved olefinic protons at τ 3.40 and 3.77, was 9.2 ± 1 (average of two determinations).

C. With Cyclohexene and Cyclohexane.—In a similar experiment using a mixture of cyclohexane and cyclohexene in a molar ratio of 10:1, an approximate value for the ratio of XVI and XV was obtained from the relative areas of the methylene doublet of XV at τ 7.25 and the aliphatic protons of XVI in the region of 7.5–9.6. A correction for the contribution of the aliphatic protons of XV to the latter area was calculated from the methylene doublet of XV. The XVI-XV ratio was found to be 2.5 ± 0.5 (average of two determinations), giving a reactivity ratio of cyclohexene-cyclohexane of 25 ± 5 after correction for the 10:1 ratio of the reactants. This value is only approximate, since it is not corrected for products of insertion into C-H bonds of cyclohexene (in pure cyclohexene the addition-insertion ratio was found to be 7.7:1).

Rates of Decomposition of I.—Consumption of IV was followed by the ultraviolet absorbance at 320 or 462 $m\mu$, which was found to vary linearly with concentration.

In the case of reaction in benzene, the rate was also followed by disappearance of the well-resolved infrared peak at 2060 cm^{-1} ($\log \epsilon$ 1.09), whose intensity was found to vary linearly with concentration.

A. In Cyclohexene.—A solution of 0.050 g of IV in 25 ml of freshly redistilled cyclohexene (preheated to 50°) was immersed in a bath at $50.0 \pm 0.1^\circ$, and 2-ml aliquots were periodically withdrawn and cooled for a few seconds in an ice bath. Accurate 1.00-ml samples were transferred from these to a 10-ml volumetric flask and immediately frozen in a Dry Ice-acetone bath. Just prior to measurement, samples were thawed and the flask was filled with anhydrous ether. Absorbance of the ether solution was measured at 320 $m\mu$ using a reference solution containing 1 ml of cyclohexene in 10 ml of ether solution. Plots of $\log A$ vs. t were linear. The first-order rate constant calculated from the slope of the plot of $\log A$ vs. t was $17.6 \times 10^{-3} \text{ min}^{-1}$ (average of three runs with a range of $3.5 \times 10^{-3} \text{ min}^{-1}$).

B. In Benzene.—The reaction of V with benzene was followed as described for cyclohexene. A solution of 1 ml of benzene in 10 ml of solution was used in the reference cell. Although the reaction products showed insignificant absorbance at 320 $m\mu$, the ether-benzene mixture absorbed considerably. Most of this interference was removed by compensation, and the remainder by subtraction of absorbance at $t = \infty$ (A_∞) from A_t . The first-order rate constant calculated from the plot of $\log A$ vs. t was $9.5 \times 10^{-3} \text{ min}^{-1}$ (average of two runs with a range $2.6 \times 10^{-3} \text{ min}^{-1}$). Representative data are reported in Table II.

TABLE II
KINETIC DATA FOR THE DECOMPOSITION OF
1,4-DIPHENYL-5-DIAZOMETHYL-1,2,3-TRIAZOLE AT $50 \pm 0.1^\circ$

In benzene			In carbon tetrachloride		
Time, min	Absorbance at 2060 cm^{-1}	$k \times 10^4, ^a \text{ min}^{-1}$	Time, min	Absorbance, $A_t - A_\infty$	$k \times 10^4, ^a \text{ min}^{-1}$
30	0.33		6	0.160	
45	0.29	8.7	9	0.150	21
60	0.255	8.5	12	0.125	61
75	0.205	14.5	15	0.080	148
105	0.161	8.3	17	0.060	143
135	0.115	11.0	19	0.045	143
165	0.090	8.2	21	0.035	125
195	0.070	8.4	23	0.025	168
	Average	8.9	25	0.020	111
				Average ^c	139

^a Calculated for each adjacent pair of points. ^b At 462 $m\mu$. ^c Over last six values.

The reaction rate was also followed by the infrared method. Samples were periodically withdrawn from the reaction mixture by means of a syringe and introduced into a 0.1-mm infrared cell. Absorbances were determined at 2060 cm^{-1} using a reference cell filled with benzene. Runs were conducted at $50.0 \pm 0.1^\circ$ and $40.0 \pm 0.1^\circ$. First-order rate constants were (50.0°) 9.2×10^{-3} and (40.0°) 2.5×10^{-3} (calculated activation energy 25.9 kcal/mol).

C. In Carbon Tetrachloride.—Owing to interfering absorbance by reaction products, measurements were made at 462 $m\mu$, using carbon tetrachloride in the reference cell and as the solvent. Plots of $\log A$ vs. t were initially nonlinear but became linear after approximately 15 min. Second-order plots of the data were also nonlinear. The first-order rate constant calculated from the linear portion of the plots was $122 \times 10^{-3} \text{ min}^{-1}$ at 50.0° , range $34 \times 10^{-3} \text{ min}^{-1}$ (average of two runs) (cf. Table I).

D. In Cyclohexane.—Owing to the limited solubility and slow rate of solution of IV in cyclohexane, it was necessary to carry out kinetic runs in mixtures containing 1:1 and 2:1 molar ratios of cyclohexane and benzene or a 2:1 molar ratio of cyclohexane and ether. Rates were affected relatively little by changes in the solvent mixture. Experiments were conducted at $50.0 \pm 0.1^\circ$ and absorbances were measured at 462 $m\mu$. First-order rate constants were $17.1 \times 10^{-3} \text{ min}^{-1}$ (2:1 cyclohexane-ether), $19.3 \times 10^{-3} \text{ min}^{-1}$ (1:1 cyclohexane-benzene), and $19.8 \times 10^{-3} \text{ min}^{-1}$ (2:1 cyclohexane-benzene), average value $18.7 \times 10^{-3} \text{ min}^{-1}$.

Reaction of 1,4-Diphenyl-5-chloromethyl-1,2,3-triazole (XXII) with Potassium *t*-Butoxide. A. In *t*-Butyl Alcohol. Bis(1,4-Diphenyl-1,2,3-triazole-5-methyl) Ether (XXIII).—A solution of 0.70 g of XXII in 75 ml of *t*-butyl alcohol containing 0.56 g of potassium *t*-butoxide was stirred at room temperature for 20 hr. A white precipitate (XXIII), 0.56 g, was collected on a filter and washed with *t*-butyl alcohol, mp 205–206°. The *t*-butyl alcohol was removed from the mother liquor, the residue extracted with benzene, and the extract washed with water and dried (sodium sulfate). Removal of benzene left 0.18 g of residue, mp 201–204°. The solids were combined and recrystallized from benzene-petroleum ether to give 0.50 g (96%) of XXIII pure by thin layer chromatography. It absorbed in the infrared at 1600, 1500, 1080, and 1000 cm^{-1} (1,4-diphenyl-1,2,3-triazolyl system) and at 1060 cm^{-1} (ether linkages). The nmr spectrum showed a singlet at τ 5.42 and a multiplet centered at 2.5, with relative areas of 1:5. An analytical sample prepared by three recrystallizations from chloroform-petroleum ether mixtures had mp 205–206°.

Anal. Calcd for $C_{30}H_{24}N_6O$: C, 74.37; H, 5.00; N, 17.35; mol wt, 484. Found: C, 74.61; H, 4.86; N, 17.64; mol wt (Rast), 493.

B. In Benzene. 1,4-Diphenyl-5-*t*-butoxymethyl-1,2,3-triazole (XXIV).—To a well-stirred solution of 1.00 g of XXII in 50 ml of anhydrous benzene was added 0.67 g of potassium *t*-butoxide. The initial red color slowly faded during 2 hr while stirring at room temperature, and disappeared completely after heating under reflux for 2 hr more. The hot solution was filtered and the benzene was removed, leaving a residue of 1.20 g, mp 140–150°. Recrystallization from benzene-petroleum ether mixture gave 0.72 g of a white, crystalline solid, XXIV, mp 151–153°. The mother liquor was chromatographed on 20 g of Florisil; 0.012 g of the starting halide, mp 115–117°, was eluted with 1% ether in benzene and 0.34 g of XXIV, mp 145–150°, was eluted with 2% ether in benzene (total yield 93%). Infrared absorptions at 1600, 1500, and 1010 cm^{-1} suggested the 1,4-diphenyl-1,2,3-triazolyl system, and strong absorptions at 1260, 1190, and 1060 cm^{-1} suggested an ether linkage. The nmr spectrum showed singlets at τ 8.74 ($-C-CH_3$) and 5.62 ($Ar-CH_2-$) and a complex multiplet centered at 2.5 (relative areas 9:2:10). An analytical sample prepared by three recrystallizations each from ethanol-water and benzene-petroleum ether mixtures had mp 151–152°.

Anal. Calcd for $C_{19}H_{21}N_3O$: C, 74.24; H, 6.89; N, 13.67; mol wt, 307. Found: C, 74.10; H, 6.82; N, 13.72; mol wt (cryoscopic in benzene), 300.

Reaction of 1,4-Diphenyl-5-chloromethyl-1,2,3-triazole (XXII) with *n*-Butyllithium.³³ 1,2-Bis(1,4-diphenyl-1,2,3-triazol-5-yl)ethane.—To a cold (10°) solution of 1.00 g of XXII in 50 ml of anhydrous benzene was added 1.8 ml of 2.0 *N* *n*-butyllithium in pentane with rapid stirring. After about two-thirds of the *n*-butyllithium was added, a precipitate began to form. The suspension was allowed to warm to room temperature and was stirred overnight. The precipitate was collected on a filter and recrystallized from benzene to give 0.74 g of white solid (XXV), mp 279–280°. Concentration of the mother liquor gave an additional 0.08 g (total yield 97%). Infrared absorption at 1600, 1500, 1080, and 1000 cm^{-1} suggested phenyl and 1,2,3-triazole

(33) General method of G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, **86**, 4042 (1964).

rings; the nmr spectrum showed a singlet at τ 7.03 and a multiplet centered at 2.6 (area ratio 1:5). No halogen could be detected by sodium fusion, and no reaction was observed with bromine or potassium permanganate. An analytical sample prepared by three recrystallizations from benzene-chloroform and one from ethanol-chloroform had mp 279–280°.

Anal. Calcd for $C_{15}H_{12}N_3$: C, 76.90; H, 5.16; N, 17.94; mol wt, 468. Found: C, 76.76; H, 5.09; N, 18.11; mol wt (Rast), 495.

Reaction of 1,4-Diphenyl-5-dibromomethyl-1,2,3-triazole (XXVI) with *n*-Butyllithium. 1,2-Bis(1,4-diphenyl-1,2,3-triazol-5-yl)ethylene (XXVII).—A solution of 2.00 g of XXVI in anhydrous ether under nitrogen was cooled to 0–5° and 3.0 ml of a 1.5 *N* pentane solution of butyllithium was added dropwise through a rubber septum by means of a syringe. The solution was stirred for 3 hr at room temperature and was then poured into ice water and extracted with benzene. The benzene extract was washed successively with 1 *N* hydrochloric acid and water, dried over anhydrous sodium sulfate, and concentrated to small volume. A white precipitate, XXVII, was collected (0.270 g), mp 236–241°. Chromatography of the mother liquor on 80 g of silica gel gave on elution with 1% ether in benzene 0.602 g of the starting dibromide XXVI (mp 144–147°), 0.30 g each of two additional unknown compounds, XXVIII (mp 220–225°) and XXIX (mp 240° with extensive decomposition), and an additional 0.179 g of XXVII, eluted in the given order. The same product mixture was obtained when reaction was carried out in benzene, cyclohexene, ether-benzene or ether-cyclohexene. No evidence was obtained for reaction with the solvent in any case.

The infrared spectrum of XXVII showed bands at 1600, 1500, 1080, and 1000 cm^{-1} (phenyl and 1,2,3-triazole rings). The nmr spectrum showed a singlet at τ 3.03 and a complex multiplet centered at 2.4, with relative areas of 1:10. Halogen could not be detected by sodium fusion; positive tests for unsaturation were obtained with both bromine and potassium permanganate. Hydrogenation of XXVII in ethyl acetate over platinum oxide gave XXV, identified by mixture melting point. An analytical sample obtained by two crystallizations each from benzene-petroleum ether and ethanol-petroleum ether mixtures, had mp 244–245°.

Anal. Calcd for $C_{15}H_{11}N_3$: C, 77.24; H, 4.75; N, 18.02. Found: C, 77.27; H, 4.71; N, 17.86.

Treatment of XXVII with bromine in chloroform solution gave XXVIII as shown by infrared spectra and mixture melting point. When XXVIII was treated with alcoholic potassium hydroxide, XXIX was produced. Heating an acetic acid solution of XXVIII with zinc dust for 3 hr gave XXVII. Both XXIX and XXVIII gave positive tests for halogen. This evidence suggests that XXVIII is 1,2-bis(1,4-diphenyl-1,2,3-triazol-5-yl)ethylene dibromide and that XXIX is the corresponding vinyl bromide.

Thermolysis of 1,5-Diphenyl-4-diazomethyl-1,2,3-triazole (XXX).—A solution of 0.500 g (0.0019 mol) of XXX in 65 ml of anhydrous benzene was heated under reflux for 5 hr with protection from oxygen. Thin layer chromatography indicated three products; vapor phase chromatography at 180° showed a single volatile product. Column chromatography on 40 g of silica gel gave 0.060 g (17%) of a white solid (XXXII), mp 115–117°, after elution with 50% benzene-petroleum ether, and 0.264 g of a white solid (XXXI), mp 310–315° dec, after elution with 50% ether-benzene.

Compound XXXII reacted readily with both bromine and potassium permanganate and gave a yellow precipitate with ammoniacal cuprous chloride. A monosubstituted acetylene

structure was supported by infrared absorptions at 3190 (3300 in chloroform solution) and 2100 cm^{-1} . The nmr spectrum showed a singlet at τ 6.87 and multiplets centered at 2.8 and 1.8 (relative areas 1:8:2). The chemical shifts and splittings of the multiplets were very similar to those of the anil of benzoyl cyanide. An analytical sample prepared by four recrystallizations from petroleum ether had mp 118.5–119.5°.

Anal. Calcd for $C_{15}H_{11}N$: C, 87.77; H, 5.40. Found: C, 87.88; H, 5.40.

A sample of XXXII was heated for 10 min with 4 *N* sulfuric acid. Steam distillation followed by extraction with ether gave phenyl ethynyl ketone, isolated as its 2,4-dinitrophenylhydrazone, mp 316° dec (lit.³⁴ mp 314° dec). Neutralization of the acid solution with sodium hydroxide followed by extraction with ether gave aniline, identified by its gas chromatographic retention time at 120°.

The infrared spectrum of XXXI showed a band at 1650 cm^{-1} , attributable to $C=N$, and bands at 1600, 1500, 1070, and 1000 cm^{-1} (phenyl and 1,2,3-triazole rings). The nmr spectrum contained a singlet at τ 1.44 and a multiplet centered at 2.9 (relative areas 1:10). Confirmation of structure XXXI was obtained by synthesis in quantitative yield from 1,5-diphenyl-1,2,3-triazol-4-carboxaldehyde and an equimolar quantity of its hydrazone. An analytical sample prepared by four recrystallizations from chloroform-petroleum ether had mp 316–318° dec.

Anal. Calcd for $C_{15}H_{11}N_4$: C, 72.86; H, 4.48. Found: C, 72.57; H, 4.64.

Similar results were obtained when XXX was decomposed by heating in freshly redistilled cyclohexane (yields: XXXII, 30%; XXXI, 66%) or in freshly redistilled cyclohexene (yields: XXXII, 12%; XXXI, 64%). No evidence was found for reaction with the solvent in any of these decompositions.

Attempted Cyclization of 1,4-Diphenyl-1,2,3-triazole-5-carboxylic Acid.—Treatment of 1,4-diphenyl-1,2,3-triazole-5-carboxylic acid* with anhydrous hydrogen fluoride (24 hr at ca. 20°) or polyphosphoric acid³⁵ (24 hr at 100°) led only to recovered starting material (94–98%).

Registry No.—IV, 15764-89-3; VII tosylhydrazone, 15764-90-6; 1,5-diphenyl-1,2,3-triazole-4-carboxaldehyde tosylhydrazone, 15764-91-7; VIII, 15764-92-8; IX, 15764-93-9; 1,5-diphenyl-1,2,3-triazole-4-carboxaldehyde hydrazone, 15764-94-0; XII, 15764-95-1; XIV, 15764-96-2; XIV (adduct with maleic anhydride), 15815-83-5; XV, 15764-97-3; XVI, 15764-98-4; XVII, 15815-84-6; XVIII, 15892-88-3; XIX, 15892-87-2; XXII, 15815-85-7; 1,4-diphenyl-5-methyl-1,2,3-triazole, 15765-00-1; XXIII, 15765-01-2; XXIV, 15765-02-3; 1,2-bis(1,4-diphenyl-1,2,3-triazol-5-yl)ethane, 15765-03-4; XXVI, 15815-86-8; XXVII, 15765-04-5; XXX, 15765-05-6; 1,4-diphenyl-5-hydroxymethyl-1,2,3-triazole, 15765-06-7; XXXI, 15765-07-8; XXXII, 15765-08-9.

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