Site Selectivity in Attack by Carbenes on Substituted Benzenes. 5-Diazomethyl-1,4-diphenyl-1,2,3-triazole[1]

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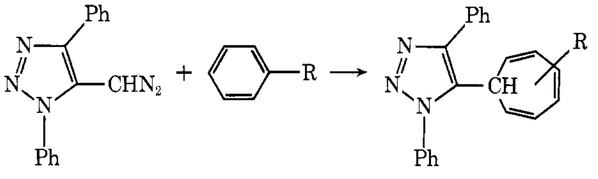
5-Diazomethyl-1,4-diphenyl-1,2,3-triazole (I) reacts with monosubstituted benzenes at 40–50° to give 72–90% yields of mixtures of 7-(1,4-diphenyltriazol-5-yl)tropilidenes in which the predominant isomer has the substituent in the 3 position (CH_3 or F) or the 2 position (CH_3O). The relative reactivities of monosubstituted benzenes toward the carbene from I were determined by competition experiments; they could be correlated by a Hammett equation in σ_p with $\sigma = -1.0$, corresponding to an electrophilic species with a selectivity more closely resembling that of carboethoxynitrene than carboethoxycarbene. 5-(α-Diazobenzyl)-1,4-diphenyltriazole thermolyzed more slowly than the diazomethyl analog, but still showed first-order kinetics with a rate constant independent of solvent in the absence of a proton source. It did not form addition or insertion products, but gave a mixture consisting principally of the symmetrical tetrasubstituted ethylene, the corresponding ethane, and 5-benzoyl-1,4-diphenyltriazole. These products, the result of dimerization, abstraction of hydrogen, and reaction with O_2, imply the intermediacy of a carbene in the triplet state.

The importance of the method of generation of a carbene on its chemical behavior has become evident in recent years. Among examples that may be cited, ethyl diazoacetate when photolyzed in cyclohexene gives addition product (7-carboethoxynorcarane) and insertion products in a ratio of 26:21, but, when the reaction is brought about by thermolysis with a copper catalyst, addition of the carbene is the only result observed.[2] The factors that have been proposed[3-6] to account for such differences are spin multiplicity, state of electronic or vibrational excitation, solvation, and coordination or other bonding to metals. Some significant studies of uncatalyzed thermolysis of diazo compounds have been made,[7] but, in view of the importance of obtaining unambiguous evidence about the behavior of carbenes, it is desirable to obtain a wider selection of observations made on carbenes generated without the aid of catalysts or similar reactants, and without high input of energy (thermal or photochemical). We have reported[8] on a carbene source that might meet these requirements: 5-diazomethyl-1,4-diphenyl-1,2,3-triazole (I). It gives products of typical carbene reactions on thermolysis only slightly above room temperature (40–50°), in the dark and in the absence of any catalyst. In certain reactions, it showed a higher selectivity than sources of methylene or carboethoxycarbene, a feature believed to be in part due to electronic stabilization of the carbene. Because its reactions included ring expansion of benzene to tropilidene cleanly and in good yield, we undertook the study reported here on its selectivity toward substituted benzenes.



I

Results and Discussion

The diazo compound I was originally prepared[8] by the Bamford–Stevens process, utilizing decomposition of the lithium derivative of 1,4-diphenyltriazole-5-carboxaldehyde *p*-toluenesulfonylhydrazone. Because this reaction was only erratically reproducible and was cumbersome in operation, we have developed a route involving oxidation of the unsubstituted hydrazone with phenyliodoso acetate, which proved superior to all conventional reagents, such as manganese dioxide or mercuric oxide, for oxidizing hydrazones, and consistently gave yields of 80% or better.

The crystalline diazo compound was dissolved in a large excess of a substituted benzene and the mixture was heated at 45–55°. A mixture of isomeric tropilidenes was obtained, from which only one component could generally be isolated by crystallization. For quantitative assay, the mixed isomers were freed from aldazine and other contaminants by column chromatography and were examined by nmr. Success of this assay depends on the sensitivity of the chemical shifts of the tropilidene protons to the substituent and of the substituent to its position, such that not all substrates that would be desirable allow the products to be assayed satisfactorily. Attempts with chromatographic or other types of spectrographic assay offered no improvement.

The products obtained from toluene illustrate the method, which is based on comparison with the known shifts[9] of the protons of tropilidene (1-H, δ 5.28 ppm; 2-H, 6.12 ppm; 3-H, 6.55 ppm; 7-H, 2.20 ppm). In the diphenyltriazolyltropilidenes, the 7 hydrogen is shifted to about 3.1 ppm by the adjacent triazolyl substituent; the five olefinic protons fall in the regions 5.82–6.42 (allylic vinyl) and 4.95–5.32 ppm (simple vinyl), and the methyl groups of the positional isomers fall at 1.97, 1.84, and 1.76 ppm. The methyl signals were assigned to the 3-, 2-, and 1-methyl isomers, respectively, according to the relative shifts of the corresponding ring protons. This assignment was confirmed by comparison with the spectrum of the one isomer that could be isolated by fractional crystallization; in the vinyl region, the relative areas of the signals at 6.14 (allylic vinyl) and 5.15 ppm (simple vinyl) were 4:1 and the methyl group must therefore occupy a 1 position (vinyl). The remaining simple vinyl proton (6-H) was coupled with 7-H (J = 3.0 Hz) and with 5-H (J = 4.6 Hz), as required.

Of the substituted benzenes used as substrates, isopropoxybenzene gave a 92% yield of isomeric tropilidenes whose nmr signals could not be accurately resolved; nitrobenzene reacted so incompletely (*ca.* 10%) as to preclude meaningful assay of the isomer ratio; and aniline and dimethylaniline followed a different reaction path, apparently starting with attack on nitrogen, and could not be made to contribute to this study. The other results are summarized in Table I.

The relative reactivities of differently substituted benzenes toward 1,4-diphenyltriazol-5-ylcarbene were deter-

Table I
Isomeric *x*-Substituted 7-(1,4-Diphenyltriazol-5-yl)tropilidenes from Monosubstituted Benzenes C_6H_5-G.

Substrate	Yield,[a] %	Isomer distribution[b] 3-G	2-G	1-G
$CH_3C_6H_5$	90	50.0	27.3	22.7
$CH_3OC_6H_5$	94	34.8	38.3	26.4
FC_6H_5	72	50.0	23.5	26.5

[a] Isolated, purified product mixture. [b] Per cent composition of purified product mixture.

mined from competition experiments, in which equimolar amounts of pairs of substrates were allowed to react with 1 molar equiv of I in sealed tubes, and the change in relative amounts of the substrates was monitored by vpc at intervals. Under these conditions, the rates relative to benzene can be calculated from the relation

$$\frac{k_{(C_6H_5G)}}{k_{(C_6H_6)}} = \log \frac{[C_6H_5G]_t}{[C_6H_5G]_{t_0}} \bigg/ \log \frac{[C_6H_6]_t}{[C_6H_6]_{t_0}}$$

The reliability of this treatment depends on freedom from extraneous losses of substrate; product assays had already shown that side reactions were minimal, and attack on the solvent (*sym*-tetrachloroethane) was negligible. Figure 1 shows plots of the relative rates as a function of the extent of reaction. The points determine straight lines from the origin; their slopes give the rates relative to benzene. The numerical results are collected in Table II, and are compared with similar data that have been reported[10] for carboethoxycarbene and carboethoxynitrene.

Although it is of uncertain justification[10] to apply Hammett substituent constants derived from electrophilic substitution reactions to ring-expansion reactions, it is practical and interesting, and previous studies in this area[10] have used them. In Figure 2, the relative rates are plotted against σ_p; the best least-squares fit is $\log k = 0.16 - 0.8\ \sigma_p$ with a probable error of 0.06 (the scatter of points is much larger with σ_m, probable error 0.25). However, trifluoromethylbenzene reacted about twice as fast as would be expected, but there were attendant analytical complications; if it is omitted from the calculations, the expression becomes $0.11 - 1.0\ \sigma_p$. Either way, the value for the Hammett regression factor qualitatively confirms that we are dealing with an electrophilic carbene; comparison with the values −0.38 reported[10] for carboethoxycarbene and −1.32 for carboethoxynitrene is especially interesting, for it demonstrates that the triazolylcarbene more closely resembles nitrenes, with their greater selectivity, than other carbenes. This fact supports the view that the triazolylcarbene is significantly stabilized by interaction with the heterocyclic ring; the possibility that the selectivity may also be influenced by the conditions used to generate the carbene is an aspect that we plan to investigate.

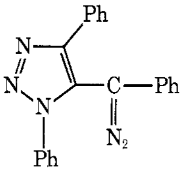
A somewhat parallel study has been made[11] of carbenoid attack on alkylbenzenes, using the very different system ethylidene iodide plus diethylzinc or diethylcadmium, which produces 7-methyltropilidenes presumably through a species related to methylcarbene. A qualitatively similar isomer ratio for toluene—22% 1-methyl, 32% 2-methyl, 46% 3-methyl—and a reactivity relative to benzene of 2.5 were found. Although the attacking species may be far from a free carbene in this system, it evidently has similar electronic demands to our triazolylcarbene. Another study,[12] in which iodoform and diethylzinc were used to convert alkylbenzenes to ethylalkyltropilidenes, reached rather different results. The major isomer obtained from toluene was the 1-methyltropilidene; however, the investigators believed that the product ratios were not determined by the initial carbenoid attack, but by a subsequent step in which a tropylium iodide reacted with ethylzinc iodide. The mobility of the iodide moiety would erase any directing effect operating in the initial attack.

Table II
Relative Rates of Attack on Substituted Benzene Substrates

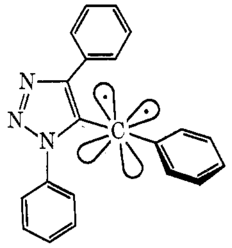
	k(Ph-G)/k(Ph-H) Diphenyltriazolylcarbene	Carboethoxycarbene	Carboethoxynitrene
i-$PrOC_6H_5$	2.03 ± 0.34[a]		
$CH_3OC_6H_5$		1.15	2.88
$EtOC_6H_5$	2.44 ± 0.53		
$CH_3C_6H_5$	2.08 ± 0.21	1.06	2.06
C_6H_6	1.00	1.00	1.00
FC_6H_5		0.80	0.62
ClC_6H_5		0.84	0.77
$O_2NC_6H_5$	0.22 ± 0.03		
$F_3CC_6H_5$	0.81 ± 0.05	0.55	0.22

[a] These deviation figures were determined graphically from plots of log ($[RC_6H_5]/[RC_6H_5]$) *vs.* log ($[C_6H_6]/[C_6H_6]$) by comparing the slopes from each point to the origin with the computed least mean squares slope.

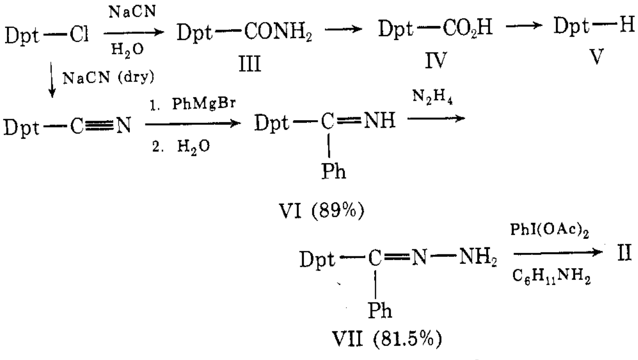
We also wished to examine the α-phenyl analog of I, 5-α-diazobenzyl-1,4-diphenyltriazole (II), which would give a carbene sterically substantially more hindered, and in which the triplet state could be expected to have increased stabilization. In the carbene from II, crowding should favor orientation of the α-phenyl group orthogonal to the triazole ring; this orientation would allow maximum overlap of the π-electron systems of the α-phenyl group and the triazole ring, respectively, with the two orthogonal p orbitals that accommodate the two unpaired electrons of the triplet state of the carbene. Furthermore, a linear orientation of the substituents in the sp-hybridized triplet carbene would entail less crowding than the *ca.* 120° angle about the sp^2, singlet carbene.



II



Diazo compound II was prepared from 5-chloro-1,4-diphenyltriazole by successive conversion to the nitrile, the phenyl ketimine, and the hydrazone (of 4-benzoyl-1,4-diphenyltriazole). Conversion of the chloride to the cyanide by reaction with sodium cyanide, a published procedure,[13] was found to be very sensitive to moisture in the solvent.



Dpt = 1,4-diphenyltriazol-5-yl

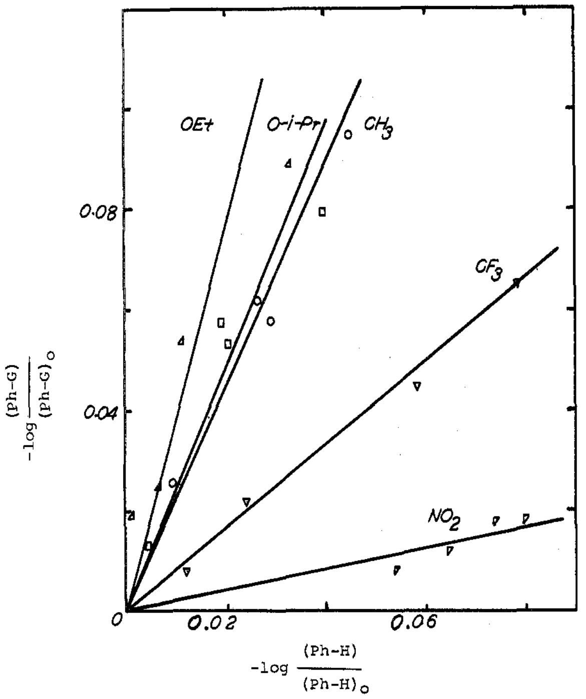


Figure 1. Relative rates from decomposition of 5-diazomethyl-1,4-diphenyl-1,2,3-triazole in aromatic substrates (Ph-G): △, G = OEt; □, G = O-*i*-Pr; ○, G = CH_3; ▽, G = CF_3; ▼, G = NO_2.

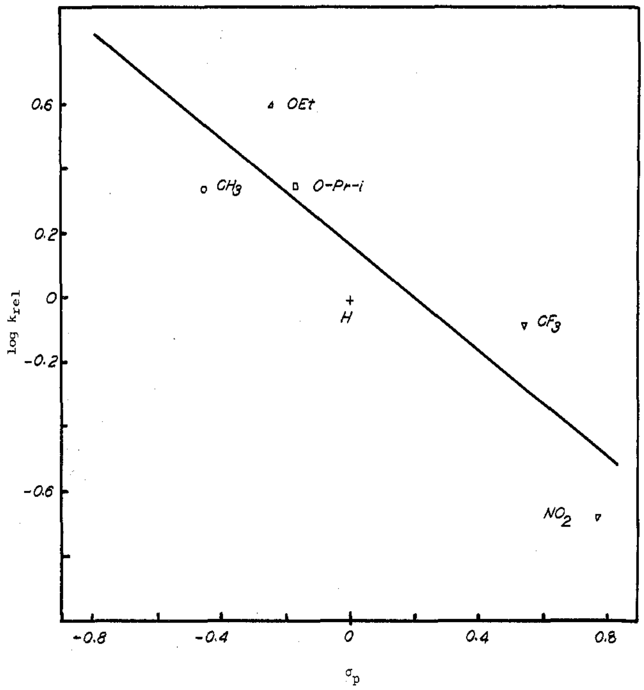


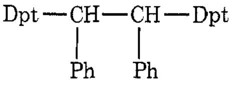
Figure 2. Plot of Hammett substituent constants, σ_p, against relative rates of reaction of aromatic substrates with 1,4-diphenyl-1,2,3-triazol-5-ylcarbene.

When dimethyl sulfoxide that was not strictly anhydrous was used, the yield of nitrile dropped sharply, and a mixture of the 5-carboxamide and 1,4-diphenyltriazole took its place. The latter was found to arise by decarboxylation of 1,4-diphenyltriazole-5-carboxylic acid, which came from hydrolysis of the amide. Other routes to II were tried without success; in particular, 5-benzyl-1,4-diphenyltriazole resisted free-radical bromination and could not be converted to the 5-(α,α-dibromobenzyl) derivative, and 5-benzoyl-1,4-diphenyltriazole resisted all attempts to convert it to its hydrazone.

Conversion of the ketimine VI to the hydrazone was slow, and was accompanied by formation of the primary amine, 5-(α-aminobenzyl)-1,4-diphenyltriazole (VIII), which was also prepared from VI by reduction with sodium borohydride. The amount of VIII was much greater in runs on a small scale; it is presumed to arise by reduction of VI by diimide formed by action of air on hydrazine (reduction of 5-benzoyl-1,4-diphenyltriazole to the carbinol upon prolonged refluxing with hydrazine has also been observed.)[14]

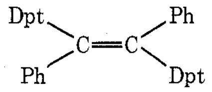
The kinetics of thermolysis of II were determined spectrophotometrically in anisole and in nitrobenzene; they were accurately first order, and the constants did not differ significantly between the two solvents (9.9 and 8.8 × 10^{-3} min^{-1}, respectively, at 70°). This is considerably slower than thermolysis of I (at 50°, k = 8.9 × 10^{-3} min^{-1}).[8] In dioxane containing traces of moisture, however, the rate was roughly 20 times as fast as in anisole or nitrobenzene and the principal product, the carbinol Dpt-CHOH-Ph, was different. These observations are consistent with the interpretation that decomposition in aprotic solvents produces a carbene, but proton sources, such as water, may catalyze a noncarbenoid reaction that may become dominant. This contrasts with the behavior observed by Bethell, Whittaker, and Callister[15] for diphenyldiazomethane, the rate of thermolysis of which in acetonitrile was not markedly accelerated by water, even though the reaction path was diverted to formation of carbinol.

The products of thermolysis in the solvents used in the kinetic experiments and in three other aromatic solvents were examined by thin layer and column chromatography, fractional crystallization, and nmr and ir. The mixtures were complex, and that from benzene showed at least eight components by tlc; some of them were dark colored, uncrystallizable materials. Only three could be obtained crystalline for identification: the symmetrically tetrasubstituted ethane IX, the corresponding ethylene X, and 5-benzoyl-1,4-diphenyltriazole (XI). These same three products were formed in each of the other aromatic solvents, as shown in Table III. The other portions of the reaction mixtures were carefully scrutinized by nmr for evidence that any compound had been formed by attack on the aromatic solvents, but none could be obtained; if addition or insertion products were indeed formed, their amounts must have been less than *ca.* 5%. The yields of IX, X, and XI were determined from the amounts isolated pure augmented by semiquantitative estimates of the amounts in the mother liquors, reckoned from the relative sizes of their tlc spots.

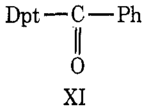


$$\underset{\text{Ph}}{\text{Dpt—CH}}\text{—}\underset{\text{Ph}}{\text{CH—Dpt}}$$

IX



X



$$\text{Dpt—}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{—Ph}$$

XI

These products, the result of abstraction of hydrogen, dimerization, and reaction with oxygen, are those typical of triplet carbenes;[16] products attributable to singlet carbenes were evidently not formed in significant quantities. Presumably the steric effect mentioned above operated to accelerate spin inversion so as to forestall competing reactions by the singlet carbene which, according to conservation of spin, must have been the initial species. The large amount of ketone XI formed in nitrobenzene might be considered anomalous, but we believe it is not; the solvents were swept with nitrogen before use, but the amount of residual dissolved oxygen was not checked, and must have been variable.

Table III
Composition[a] of Products of Thermolysis of 5-Diazobenzyl-1,4-diphenyltriazole (II)

Solvent	IX, %	X, %	XI, %
Benzene	42.4	5.5	6.7
Toluene	38.0	12.3	12.5
Anisole	55.2	5.5	4.7
Isopropoxybenzene	46.2	3.0	10.9
Nitrobenzene	39.3	0	25.6

[a] Estimated error between 0 and ±2.1.

The complete absence of the ketazine from the thermolysis products was surprising, for ketazines are generally formed from diazoalkanes and their high melting points and low solubility make the isolation of even small amounts easy. We could not check the possibility that the ketazine was converted to the symmetrical ethylene X by reaction with diazo compound, because the precursors, such as the ketone and hydrazone, were so unreactive that the ketazine could not be prepared by any means. However, the proclivity of hindered diazo compounds to form ethylenes by dimerization of carbenes, rather than forming azines, has been reported by Zimmerman and Paskovich.[17] If formation of azine depends on reaction of singlet carbene with diazoalkane, as appears to be the case,[15] rapid spin inversion to the triplet would suppress it, as would steric hindrance. By contrast, thermolysis of I gives aldazine in 8–14% yields.

The effect of changing from phenylcarbene to diphenylcarbene, previously reported[16,18] on the basis of photolysis and thermolysis of the diazo compounds, and inferred to result from reaction of the carbenes respectively in the singlet and triplet states, is thus confirmed in this parallel instance.

Experimental Section[19]

1,4-Diphenyl-1,2,3-triazole-5-carboxaldehyde Hydrazone. This preparation utilized the finding by Barton, O'Brien, and Sternhall[20] that formation of azine during conversion of aldehydes to hydrazones is greatly reduced in the presence of triethylamine. To a hot solution of 5 g (0.02 mol) of 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde[14] in 350 ml of absolute ethanol were added 14 ml of triethylamine and 28 ml of 95%+ hydrazine, in that order. The solution was allowed to reflux for 1 hr, and was then concentrated under reduced pressure to *ca.* 100 ml; about 800 ml of ether was added; and the solution was poured into 800 ml of water and extracted. The ethereal layer was washed with five 250-ml portions of water and was then dried ($CaCl_2$); removing the ether under aspirator vacuum left a colorless, viscous oil, which according to tlc was at least 80% hydrazone (ir spectrum identical with that of authentic material[14]). The oil could be crystallized from aqueous ethanol, but losses due to formation of azine were large. Therefore, the oil was oxidized to I immediately.

5-Diazomethyl-1,4-diphenyl-1,2,3-triazole (I). The oily hydrazone from 5 g (0.01 mol) of aldehyde was dissolved in 40 ml of methylene chloride and 5.1 ml (3.965 g, 0.04 mol) of cyclohexylamine, and the solution was cooled to −10°. A solution of 6.44 g (0.02 mol) of (diacetoxyiodo)benzene (phenyliodoso acetate)[21] in 85 ml of methylene chloride was added with stirring at a rate such that the temperature was maintained at −5 ± 2°. The mixture was stirred for an additional 1 hr at about 0°, and was then cooled to −25° and filtered. The filtrate was extracted with four 100-ml portions of ice–water, and was then dried ($CaCl_2$). The solvent was removed *in vacuo* without external warming, leaving a dark brown oil; trituration with 70 ml of ether precipitated 2.65 g of bright orange solid, mp 101° (ir spectrum and tlc behavior identical with those of I).[14] The overall yield from aldehyde was 49%.

1,4-Diphenyl-1,2,3-triazole-5-carboxamide (III). Using the procedure of Friedman and Shechter,[13] but with dimethyl sulfoxide from a partly used bottle, and thus presumably moist, there was obtained 2.28 g (58%) of a white solid, mp 210–215°, from 4.00 g (0.0157 mol) of 5-chloro-1,4-diphenyl-1,2,3-triazole and sodium cyanide: ir 3500, 3330, and 3150 ($-NH_2$), 1675 (amide C=O), 1600 and 1500 (phenyl), and 925, 1005, and 1075 cm^{-1} (triazole). A sample recrystallized from aqueous ethanol had mp 217–219°.

Anal. Calcd for $C_{15}H_{12}N_4O$: C, 68.13; H, 4.57; N, 21.20. Found: C, 68.00; H, 4.51; N, 21.12.

This substance was identified as 1,4-diphenyl-1,2,3-triazole-5-carboxamide by acid-catalyzed hydrolysis; 1.00 g (0.00375 mol) was refluxed for 1 hr in 50 ml of 75% glacial acetic acid containing 10 ml of concentrated sulfuric acid. After conventional work-up, there was obtained 815 mg (79.6%) of recovered amide (mmp 216–218°) and 170 mg (17.1%) of 1,4-diphenyl-1,2,3-triazole-5-carboxylic acid, mp 172–173.5° with gas evolution and resolidification, remelting at 185–186° (lit.[22] mp 177° dec, remelting at 185°), mmp 173–175 and 185–186°.

5-Benzimidoyl-1,4-diphenyl-1,2,3-triazole (VI). To a solution of phenylmagnesium bromide prepared from 2.675 g (0.11 mol) of magnesium and 17.272 g (0.11 mol) of bromobenzene in 55 ml of ether was added a solution of 12.3 g (0.05 mol) of 1,4-diphenyl-1,2,3-triazole-5-carbonitrile in *ca.* 600 ml of ether. Reflux was maintained for 48 hr, after which the mixture was cooled and treated with 20 ml of absolute methanol; stirring was continued for an additional 1 hr. The magnesium salts were separated by filtration and were triturated repeatedly with fresh aliquots of methylene chloride. The combined filtrates were evaporated to leave a white solid. Recrystallization from absolute ethanol gave 14.42 g (89%) of fine, cream-colored needles: mp 149–150°; ir (Nujol) 3260 (NH), 1600 and 1500 (phenyl), 875, 1000, and 1155 cm^{-1} (triazole); nmr ($CDCl_3$) δ 7.55 (m, 15 H, aromatic) and 6.75 ppm (s, 1 H); *m/e* 324. Four recrystallizations from absolute ethanol gave an analytical sample.

Anal. Calcd for $C_{21}H_{16}N_4$: C, 77.74; H, 4.97; N, 17.28. Found: C, 77.68; H, 5.05; N, 17.33.

5-Benzoyl-1,4-diphenyl-1,2,3-triazole Hydrazone (VII). To a hot solution of 10.0 g (0.0309 mol) of VI in 380 ml of absolute ethanol was added 60 ml (1.896 mol) of anhydrous hydrazine[23] and the mixture was heated at reflux. The total time required for complete conversion of VI to VII varied between 20 and 130 hr, which made it necessary to follow each run by tlc. Upon completion, the mixture was cooled and then concentrated under reduced pressure; crystallization was completed overnight at 0°. The white hydrazone was recrystallized from absolute ethanol, affording 9.04 g (81.5%) of white, shiny platelets: mp 169–172°; ir (Nujol) 3400, 3280, and 3200 (2 NH), 1635 (C=N), 1600 and 1500 (phenyl), and 780, 1000, and 1075 cm^{-1} (triazole); nmr ($CDCl_3$) δ 7.6 (15 H, aromatic) and 6.3 ppm (s, 2 H, NH_2). The yields were consistently 72–83% of once recrystallized material and were independent of the specific reaction time. However, when hydrazone formation was attempted on 1 g or less of imine, it was significantly suppressed by a competing side reaction leading to 5-aminobenzyl-1,4-diphenyl-1,2,3-triazole. An analytical sample of VII hydrazone was obtained by three more recrystallizations from absolute ethanol.

Anal. Calcd for $C_{21}H_{17}N_5$: C, 74.31; H, 5.05; N, 20.64. Found: C, 74.26; H, 5.18; N, 20.65.

5-Aminobenzyl-1,4-diphenyl-1,2,3-triazole. In an analogous experiment with 500 mg (0.00155 mol) of VI and anhydrous hydrazine in 25 ml of ethanol, refluxed for 130 hr, the evidently impure crude solid product was taken up in ether and extracted three times with 5% HCl and once with water. The dried (Na_2SO_4) ether layer yielded 302 mg (57.5%) of pure VII. The acidic extracts were neutralized with $NaHCO_3$ and extracted with ether. Evaporation of the dried (KOH) extracts left 115 mg (22%) of white solid, mp 138–139°. This substance formed a base-soluble benzenesulfonamide, and evolved nitrogen with nitrous acid: nmr ($CDCl_3$) δ 7.8 (complex m, 15 H), 5.8 (s, 1 H), and 1.8 ppm (broadened singlet, 2 H); ir (Nujol) 3275 and 3350 ($-NH_2$), 1600, 1500 (phenyl), and 775, 1000, and 1080 cm^{-1} (triazole); *m/e* 326. The nmr signal at 1.8 ppm disappeared after treatment with D_2O. Reduction of VI with $NaBH_4$ gave the identical substance. A sample recrystallized (EtOH) five times had mp 136.5–139.5°.

Anal. Calcd for $C_{21}H_{18}N_4$: C, 77.27; H, 5.56; N, 17.17. Found: C, 77.02; H, 5.60; N, 17.27.

5-Diazobenzyl-1,4-diphenyl-1,2,3-triazole (II). A solution of 9.00 g (0.0265 mol) of VII in 75 ml of methylene chloride and 7.36 ml (0.058 mol) of cyclohexylamine was cooled to −80°, and a solution of 9.34 g (0.029 mol) of (diacetoxyiodo)benzene in 100 ml of methylene chloride was added with stirring while the temperature was maintained between −10 and −5°. Stirring was continued for 2 hr at −10 to −5°. The deep red mixture was then chilled to −30° and filtered to remove cyclohexylammonium acetate, and the precipitate was washed with small portions of chilled methylene chloride until the washings were colorless. The filtrate was concentrated to about one-half the original volume on a rotary evaporator without warming, and was again cooled to −30° for several hours. Filtration removed all residual cyclohexylammonium acetate and excess oxidizing agent, and the solution was then evaporated at room temperature, leaving a bright reddish-brown residue. Trituration with about 30 ml of ether precipitated a brick-red solid, which was washed with a small amount of ether and recrystallized from ether by dissolving it at room temperature and cooling for 48 hr at −30°, yield 5.02 of reddish-brown, irregular crystals. Three additional crops, together 1.285 g, were collected. All four fractions were pure by tlc. An additional 353 mg was obtained by chromatography of the crude filtrate on a water-jacketed column of Florisil, the red material being eluted with a petroleum ether (bp 30–60°)–ether mixture (9:1), total yield of once-recrystallized product 6.76 g (75.5%).

The nmr spectrum of the red solid showed only aromatic protons centered at 7.4 ppm. The infrared (Nujol) had a very strong, sharp peak at 2050 cm^{-1} ($N\equiv N$), also absorption at 1600 and 1500 (phenyl) and at 765, 920, and 1000 cm^{-1} (triazole). Spectral evidence thus clearly indicated the red solid to be 5-diazobenzyl-1,4-diphenyl-1,2,3-triazole (II).

The melting point of the diazo compound varied considerably from one fraction to another, and usually was not sharp. Also, when the compound was recrystallized slowly at 0°, two different types and colors of crystals became distinguishable: ruby-red transparent prisms (mp 125° with visible decomposition from 114°) and orange lumps or rosettes (mp 205°, with visible decomposition from 114°). Slow crystallization produced a larger amount of prisms, generally accompanied by some of the orange material. The two were identical with respect to their nmr (m, 7.4 ppm) and ir spectra (2050, 1600, 1500, 1000, 920, 765 cm^{-1}), their tlc values, and their chemical behavior. A solution of red prisms could easily be crystallized at −30° to give only orange rosettes, but the conversion back to prisms was more difficult. Thus, it took five slow recrystallizations, each time removing manually any prisms formed, to collect 140 mg of the latter from 217 mg of rosettes.

A sample was recrystallized at 0° five times; rosettes were removed manually from prisms and the two fractions were analyzed separately.

Anal. Calcd for $C_{21}H_{15}N_5$: C, 74.75; H, 4.48; N, 20.76. Found (prisms): C, 74.66; H, 4.51; N, 20.84. Found (rosettes): C, 74.74; H, 4.51; N, 20.88.

Thermolysis of 1,4-Diphenyl-5-diazomethyl-1,2,3-triazole (I). Solutions ranging in concentration from 0.01 to 0.02 *M* were prepared in carefully dried equipment by dissolving the diazo compound in a substituted benzene substrate, which had previously been flushed with dry nitrogen for a minimum of 1 hr. The resulting bright red or yellow solutions were immersed in an oil bath preheated to 45–55° and stirred mechanically while being kept under a positive pressure of nitrogen. The decompositions were complete after 4 hr. The work-up procedures differed for each substrate.

A. In Toluene. Thermolysis of 1.044 g (0.004 mol) of I in 200 ml of toluene gave a bright yellow solution, which was filtered to remove a very small amount of azine and was concentrated on a rotary evaporator to a viscous yellow oil, which was chromatographed on a column packed with 70 g of Florisil (100–200 mesh). Each fraction was examined by tlc as it was eluted from the column and the ones with similar composition were combined. Six fractions were obtained. The first two contained only small amounts of unidentified materials and were discarded. Fractions 4 and 5 (eluted with chloroform) and 6 (eluted with ethanol) contained only negligible amounts of mixtures of up to six compounds, three of which had been introduced with the diazo compound. No attempts were made to isolate or identify these beyond examining their nmr spectra for the presence of the potential product of C–H insertion, 1-(1,4-diphenyl-1,2,3-triazol-5-yl)-2-phenylethane, which proved to be absent.

Fractions 2 and 3 (eluted with benzene) amounted to 1.28 g (90.6%) of a pale yellow glass (X), which showed one elongated spot on tlc, and contained the three positional iosmers of *x*-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene: nmr δ 7.85 (m, aromatic, 2 H), 7.32 (m, aromatic, 8 H), 6.14 (m, $C{=}CHC{=}C$), 5.15 (m, $C{=}CHC$–), and 3.1 ppm (m, tertiary H, 1 H). The relative area of the combined vinylic signals was 5. The methyl groups appeared as singlets at 1.97, 1.84, and 1.76 ppm, with a combined relative integration of 3. The infrared spectrum (Nujol) had major absorptions at 1601 and 1505 (phenyl) and also at 1076 and 1000 (very strong), and 920 cm^{-1} (triazole).

The ratio of the isomeric cycloheptatrienes was determined in a separate experiment, in which 0.131 g (0.50 mol) of analytically pure 5-diazomethyl-1,4-diphenyl-1,2,3-triazole was thermolyzed in 50 ml of spectral-grade toluene. The viscous distillation residue was extracted with three portions of chloroform, and the extracts were dried ($MgSO_4$) and evaporated to leave 145 mg (89%) of pale yellow, viscous oil, which according to tlc was >95% cycloheptatrienes. The nmr spectrum corresponded to a mixture of 50.0% of 3-methyl-, 27.3% of 2-methyl-, and 22.7% of 1-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene. The relative amounts were determined from the intensity of the respective methyl signals (2.2:1.2:1.0). The accuracy of these determinations was confirmed by the ratio of the vinylic hydrogens, calculated from the given composition as 3.227 for the hydrogens in the 2, 3, 4, and 5 positions and 1.773 for the 1 and 6 hydrogens; the corresponding multiplets at 6.14 and 5.15 ppm had an intensity ratio of 3.2:1.8.

The chromatographically pure mixture of the three isomers was fractionally crystallized from ethanol-water, the composition of each solid fraction was examined by nmr, and those of similar isomer ratio were combined and recrystallized from ethanol or methanol. After this had been repeated seven times, 60 mg of 1-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene was obtained free from the other two isomers. Two additional recrystallizations from methanol furnished 35.4 mg of sand-colored, transparent prisms, mp 161–163°.

Anal. Calcd for $C_{22}H_{19}N_3$: C, 81.20; H, 5.99; N, 12.91. Found: C, 81.07; H, 5.98; N, 12.87.

B. In Anisole. Decomposition of 0.131 g (0.50 mol) of I in 50 ml of freshly distilled anisole resulted in a yellow solution, which was steam distilled to remove the anisole. The residue was extracted exhaustively with chloroform. The yellow oil (183 mg) obtained after drying (Na_2SO_4) and concentrating the combined extracts was purified further by preparative thin layer chromatography on silica gel, from which 161 mg (94.3%) of very pale yellow, viscous oil was obtained. It gave only one spot on tlc, decolorized bromine in carbon tetrachloride, and reduced aqueous potassium permanganate. Its nmr spectrum was consistent with a mixture of the three positional isomers of *x*-methoxy-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene: δ 7.83 (m, 2 H), 7.37 (m, 8 H), 5.0–6.4 (m, 5 H), 3.63 (s, 3-CH_3O), 3.56 (s, 2-CH_3O), 3.31 ppm (s, 1-CH_3O) superimposed on a broad hump (7-CH) (3.63–3.31 total intensity, 4 H). After the contribution by the C-7 hydrogen was subtracted, the relative areas of the methoxy signals were 1.32:1.47:1.0, corresponding to 34.8% of 3-methoxy-, 38.8% of 2-methoxy-, and 26.4% of 1-methoxy-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene.

In another experiment, 0.522 g (0.002 mol) of I yielded a brown oil, from which was separated 599 mg of pure *x*-methoxy-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene mixture by column chromatography on 25 g of Florisil. This oil was very resistant to crystallization, but after a solution of it in benzene–petroleum ether was left undisturbed at −20° for 5 months, partial crystallization took place. The solid thus obtained had nmr δ 3.31 ppm (s, 1-CH_3O); three recrystallizations from ethanol afforded 26.7 mg of white needles, mp 169–170°, of 1-methoxy-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene.

The oil recovered from the filtrate was again dissolved in benzene–petroleum ether and allowed to crystallize at 0°. The second crop thus obtained was shown by nmr to be a mixture of all three isomers, with the 3-methoxy isomer predominating (about 75%). One recrystallization from ethanol gave pure 3-methoxy-7-(1,4-diphenyl-1,2,2-triazol-5-yl)cycloheptatriene as pale cream-colored needles, mp 134.5–135.5°, nmr δ 3.63 ppm. Both samples showed compatible infrared spectra: 3000, 1625, 1605, 1505, 1080, 1000, and 925 cm^{-1}.

Anal. Calcd for $C_{22}H_{19}N_3O$: C, 77.30; H, 5.61; N, 12.31. Found (3-CH_2O isomer): C, 77.17; H, 5.56; N, 12.34. Found (1-CH_3O isomer): C, 77.38; H, 5.60; N, 12.46.

C. In Isopropoxybenzene. Thermolysis of 0.522 g (0.002 mol) of I in 50 ml of freshly distilled isopropoxybenzene, after steam distillation, extraction of the residue with chloroform, drying, and evaporation, gave 752 mg (92%) of brown oil, about 90% of which showed as one spot by the tlc.

The nmr spectrum was in good agreement with a mixture of isomeric *x*-isopropoxy-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatrienes: δ 7.86 (m, 2 H), 7.32 (m, 8 H), 7.0 (m, 5 H), 3.15 (m, 1 H), 3.28 (m, 1 H), and 1.17 ppm (three overlapping doublets, total 6 H).

When the oil was dissolved in methylene chloride, 4.3 mg of 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde azine, mp and mmp 298–302°, remained. The filtrate was evaporated and the residual oil was dissolved in a small amount of ethanol and allowed to stand at room temperature for 1 week. A small amount of white crystals had separated; the nmr spectrum suggested that they were an approximately 1:1 mixture of two isomers of *x*-isopropoxy-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene. Two more crops (136 mg) of white prisms, mp 165–169°, were obtained from the ethanolic filtrate. The chemical shifts of the methyl groups were too close to permit unequivocal differentiation of the isomers by nmr. Four recrystallizations of the first crop from ethanol afforded 6.6 mg of fine, white needles, mp 134–137°.

Anal. Calcd for $C_{24}H_{23}N_3O$: C, 78.02; H, 6.28; N, 11.38. Found: C, 77.98; H, 6.26; N, 11.31.

D. In Nitrobenzene. Thermolysis of 0.130 g (0.001 mol) of I in 25 ml of nitrobenzene gave a reddish-brown solution, which was freed from nitrobenzene by steam distillation. The residue was extracted with chloroform, and the extracts were combined, dried (Na_2SO_4), and evaporated to leave a dark brown oil, which on tlc examination revealed the presence of at least nine components, none of which amounted to more than 25% of the total mixture. Separation by preparative tlc on silica gel furnished only the component of highest R_f in reasonably pure form. Recrystallization of this fraction from benzene afforded 20.8 mg (16.8%) of a white solid, mp 172–174°, identified as 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde[8] (nmr, ir, mixture melting point). Another tlc fraction contained 43 mg of material whose nmr spectrum exhibited olefinic protons with chemical shifts expected for substituted cycloheptatrienes, but attempts at purification were foiled by rapid decomposition.

E. In Fluorobenzene. The mixture from thermolysis of 0.533 g (0.002 mol) of I in 75 ml of fluorobenzene was concentrated under aspirator pressure, leaving a dark brown oil, which was dissolved in methylene chloride and filtered to remove 6 mg of 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde azine. The fluorine nmr of the filtrate exhibited six structured singlets (sweep width 100 ppm) at 97.5, 101.8, 113.0, 114.9, 115.7, and 117.9 ppm upfield from the external standard, trichlorofluoromethane. The resonances at 113, 115.7, and 117.9 ppm were later proven to be impurities contained in the "reagent-grade" fluorobenzene; they were separated from the main product by dry-column chromatography[24] on alumina.

The major component was contained in three fractions sectioned off the column, although the last one of these was contaminated with four unidentified compounds. The first two fractions contained 473 mg (72%) of chromatographically pure product. Its spectral characteristics were in accord with a mixture of the three isomeric fluoro-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatrienes: ir ($CHCl_3$) 3050 (aromatic CH), 1640 and 1504 (phenyl), and 1000 and 1075 cm^{-1} (triazole); nmr δ 7.9 (m, 4 H), 7.4 (m, 1 H), 6.2–5.33 (m, 5 H), and 3.18 ppm (broad, 1 H). The fluorine nmr exhibited three structured singlets (sweep width 100 ppm) at 97.6, 101.8, and 114.9 ppm upfield from the external standard, trichlorofluoromethane, in a ratio of 2.1:1:1.1, nearly the same ratio as had been found for the equivalent peaks in the crude product mixture.

This mixture of isomeric *x*-fluoro-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatrienes was taken up in a small volume of ethanol and the solution was allowed to crystallize. Three successive crops were collected, amounting to a total of 323 mg. The first of these was recrystallized twice from ethanol, producing small, pale yellow leaflets, mp 141–145°, of analytical purity, but its positional identity remained spectroscopically ambiguous.

Anal. Calcd for $C_{21}H_{16}N_3F$: C, 76.54; H, 4.90; N, 12.76. Found: C, 76.55; H, 4.92; N, 12.76.

Attack of I on Substituted Benzenes. Relative Rates. The thermolyses were conducted in tubes of Vycor glass, 5 mm in diameter and 9–10 cm long. Prior to use they were cleaned with chromic-sulfuric acid solution, followed by 10 *N* sodium hydroxide, and were then rinsed repeatedly with distilled water, baked for 24 hr at about 150°, and stored in a desiccator over phosphorus pentoxide.

The solvent was commercial 1,1,2,2-tetrachloroethane, which after four fractional distillations still contained an impurity of higher R_f; although it amounted to at most 0.5%, its appearance in the vpc trace was prominent, since the solvent-substrate ratio used was larger. Since additional redistillation did not noticeably improve the purity, and the foreign component did not interfere with the vpc traces of the substrates used, the solvent was used in this state.

The aromatic substrates used were reagent-grade benzene, toluene, trifluoromethylbenzene, and phenetole, which were fractionally distilled and stored over sodium sulfate; reagent-grade nitrobenzene, which was steam distilled, dried, and then fractionally distilled; and isopropoxybenzene, which was synthesized from isopropyl bromide and sodium phenoxide, and redistilled (bp 177°). The purity of each solvent was ascertained by vpc.

Solutions were prepared by weighing approximately 0.25 mmol each of benzene and substituted benzene from a 0.24-ml syringe into a 1-ml volumetric flask, which was then filled to the mark with 1,1,2,2-tretrachloroethane, stoppered, and shaken to thoroughly mix the liquids. Half of this solution was withdrawn into a 0.5-ml syringe and added to an ampoule containing 0.0655 g (0.25 mmol) of I. The remaining half was refrigerated in the stoppered flask, until used to assay the amount of the substrates by vpc. The solution was distributed among five reaction tubes, frozen in Dry Ice-acetone, and sealed. All transfers were conducted as rapidly as possible to minimize loss of solvents. The diazotriazole used had been recrystallized from ether-petroleum ether to analytical purity.

Anal. Calcd for $C_{15}N_{11}N_5$: C, 68.94; H, 4.25; N, 26.81. Found: C, 68.91; H, 4.22; N, 26.94.

The samples were allowed to warm to room temperature and were equilibrated in a constant-temperature bath at 50.0 ± 0.1°. Tubes were withdrawn at various time intervals and were stored in Dry Ice-acetone until analyzed; one vial, "t_∞," was not removed until at least 10 hr.

The changes in composition of the samples were determined on an F & M Model 500 gas chromatograph equipped with a Brown recorder and disc chart integrator, using a 0.25 in. × 8 ft column of 5% SE-30 silicone rubber on Chromosorb 60/80 W (He flow rates 50–80 ml/min; initial temperature 30–50°; programs 0–7.9°/min). The average numerical values obtained (each an average of five measurements) were divided by the value for the t_0 sample. The best least-squares fit to a straight line for log ([Ph-G] at t_n/[Ph-G] at t_0) for the substituted substrate against log ([Ph-H] (t_n)/[Ph-H] (t_0) for benzene was caluclated by computer, according to the equation

$$k_{\mathrm{rel}} = \frac{k[\mathrm{Ph-G}]}{k[\mathrm{Ph-H}]} = \frac{\log\,([\mathrm{Ph-G}]_{t_n}/[\mathrm{Ph-G}]_{t_0})}{\log\,([\mathrm{Ph-H}]_{t_n}/[\mathrm{Ph-H}]_{t_0})}$$

The evaluation of the vpc traces of samples containing trifluoromethylbenzene was complicated by the near coincidence of the retention times of the substrate and of an undetermined reaction product which was formed in similar amounts in all experiments, regardless of the aromatic substrate, amounting to about 8%. A correction was made by subtracting the amount formed in experiments without trifluoromethylbenzene.

The overall results are presented in Figure 1 and Table II.

Kinetics of Thermolysis of 5-Diazobenzyl-1,4-diphenyl-1,2,3-triazole (II). The thermolysis rates of II were determined by observing the change in absorbance at 495 nm on a Cary 14 recording spectrophotometer. The validity of Beer's law was confirmed on five standard solutions of II in anisole; molar extinction coefficients were determined to be 69 for anisole solutions, 76 for nitrobenzene solutions, and 63 for dioxane solutions.

Method A. Solutions of II (0.012–0.015 *M*) were immersed in a water bath preequilibrated at the required temperature; 12–15 min was allowed for the solution to warm, after which time the first aliquot was removed and transferred to a cell chilled in ice-water (duration less than 15 sec). Subsequent aliquots were removed in like manner at appropriate time intervals. Absorbances were determined after each sample had cooled to room temperature.

Method B. The solution was apportioned among 12 stoppered tubes which were immersed into the equilibrated water bath. The first tube was withdrawn 10 min after immersion, and one tube each at appropriate time intervals. The sample tubes were stored in ice-water until the spectra could be scanned, for which purpose the contents were allowed to thaw, and were then transferred to the absorbance cell.

The measurements were carried out in every case by scanning the spectrum from 600 to 400 nm and determining the absorbance at the maximum (about 495 nm). Baseline corrections were applied as necessary. Decomposition to completion in *p*-dioxane resulted in a colorless solution; thus there was no interference from products. With the aromatic substrates, however, absorption caused by the yellow products began to overlap with the absorbance at 495 nm after about two half-lives, but they presented no problem during the initial period, during which the kinetic measurements were taken.

The data were evaluated by a computerized least squares fit analysis[25] to determine the coefficients for the best quadratic equation fitted to the sets of logarithm *vs.* time and the standard deviation of the log A values from the calculated straight line. In anisole, at 69.9 ± 0.1°, $k = (9.89 \pm 0.06) \times 10^{-3}\ \text{min}^{-1}$ (two experiments, 11 measured points for each); at 80.0 ± 0.1°, $k = (29.5 \pm 0.9) \times 10^{-3}\ \text{min}^{-1}$, in nitrobenzene at 70.0 ± 0.1°, $k = 10^{-3}\ \text{min}^{-1}$, and at 59.9 ± 0.1°, $k = (80.3 \pm 5.2) \times 10^{-3}\ \text{min}^{-1}$.

1,4-Diphenyl-5-(α-hydroxybenzyl)-1,2,3-triazole. Reduction of 3.5 g of XI was brought about by treatment with 0.234 g of lithium aluminum hydride in 180 ml of tetrahydrofuran at reflux for 1 hr. After conventional work-up, 2.18 g (60%) of white crystals of 1,4-diphenyl-5-(α-hydroxybenzyl)-1,2,3-triazole, mp 172–177°, clearly distinguishable by tlc from the original ketone, was obtained: ir (Nujol) 3300 and 3175 (OH), 1600 and 1503 (phenyl), 1000 and 1075 cm^{-1} (triazole); nmr 7.2 (m, 15), 6.21 (d, 1), and 3.47 ppm (d, 1). When the sample was shaken with D_2O, the 3.47-ppm doublet collapsed to a singlet. This substance was identical with the product of thermolysis of II in dioxane. An analytical sample was prepared by five more recrystallizations from benzene as shiny white needles, mp 177–179°.

Anal. Calcd for $C_{21}H_{17}N_3O$: C, 77.04; H, 5.23; N, 12.84. Found: C, 76.82; H, 5.13; N, 12.83.

The mother liquors were shown by tlc to consist of a mixture of starting material and product.

Thermolyses of 5-Diazobenzyl-1,4-diphenyl-1,2,3-triazole in Aromatic Solvents. Thermolysis of II. Solutions of II, *ca.* 0.02 *M*, in a given solvent were flushed with dry nitrogen for 30 min to 5 hr and were then heated at 80–85° in an oil bath, with stirring, in apparatus dried by baking for 12 hr, under a positive pressure of nitrogen. Decomposition was allowed to proceed for 4–5 hr, after which no more II was detectable by tlc or ir. Decompositions in benzene required a reflux condenser.

A. In Benzene. The yellow solution resulting from decomposition of 0.450 g of II in 133.4 ml of dry benzene was concentrated *in vacuo* to a yellow oil, which on trituration with ether precipitated 195.5 mg of a white solid: mp 148–198°; ir 1610, 1580, and 1500 (phenyl), 1080, 1005, and 925 cm^{-1} (triazole); nmr δ 7.87 (m, 2), 7.39 (m, 13), and 5.37 ppm (s, 1); mass spectrum m/e 310 ($C_{21}H_{16}N_3$). The empirical formula corresponds to α-(1,4-diphenyl-1,2,3-triazol-5-yl)benzyl radical, and the ir and nmr spectra unambiguously indicate the preservation of the 1,4-diphenyl-1,2,3-triazole moiety. Presumably, the compound is the dimer, 1,2-diphenyl-1,2-di(1,4-diphenyl-1,2,3-triazol-5-yl)ethane, $C_{42}H_{32}N_6$, in which the lability of the central bond is high enough to permit complete dissociation of the molecular ion under the conditions used (60 eV, direct inlet at 150–200°). Attempts to obtain a mass spectrum at lower ionization voltages gave unsatisfactory results. The structure assignment of IX is supported by the fact that the same substance was formed regardless of the aromatic decomposition medium; so it could only have been derived from II.

Eight recrystallizations from ethanol gave an analytically pure sample as fine, pure white needles, mp 221–223°.

Anal. Calcd for $C_{42}H_{32}N_6$: C, 81.25; H, 5.19; N, 13.55. Found: C, 81.13; H, 4.97; N, 13.52.

The ethereal filtrate from the foregoing fraction was concentrated and again triturated with ether to produce an additional 75 mg of IX (ir, tlc, mixture melting point). The mother liquors from this second crop were subjected to preparative tlc on silica gel. Nine bands were collected, containing a least seven compounds. The fifth band consisted of two compounds in approximately equal amounts, one of which was IX. Recrystallization from ethanol gave 9.8 mg of IX, increasing the total amount isolated to 412 mg (65.2%).

Bands 3 and 4 contained 53.8 mg of mixtures of compounds, with one material predominating to the extent of 80% as estimated from the relative intensities on tlc. A 20-mg crop (4.5%) of this material, mp 177–180°, was obtained chromatographically pure by crystallization from absolute ethanol. One further recrystallization led to pale yellow prisms of XI, mp 182–184°, identical by mixture melting point, ir, and nmr with authentic material.

Trituration with ether of the material separated in the seventh band precipitated 8.7 mg of X as white needles, mp 261–277° dec; recrystallization from ethanol increased the melting point to 297–301°, mass spectrum m/e 618 ($C_{42}H_{30}N_6$). All isolated fractions of X were combined and recrystallized repeatedly from ethanol, affording 5.0 mg of glossy white needles, mp 303–304.5°; it did not decolorize bromine in carbon tetrachloride, which is not unusual for a highly hindered olefin.

Anal. Calcd for $C_{42}H_{30}N_6$: C, 81.53; H, 4.89; N, 13.59. Found: C, 81.33; H, 5.09; N, 13.60.

Approximate estimates of the total amounts of products formed were obtained by examining the various impure fractions by tlc and estimating the proportion of each component from the relative size of the spot on the chromatogram. The residual fractions were deduced to contain approximately 15 mg of XI, 18 mg of IX, and 28 mg of X; adding the actually isolated quantities to these amounts gave 44 mg of XI (6.7%), 271 mg of IX (42.), and 37 mg of X (5.5%). None of the other compounds observed as tlc spots was obtained in quantities sufficient for isolation and identification.

B. In Toluene, Anisole, Isopropoxybenzene, and Nitrobenzene. Thermolyses in these solvents were examined in much the same way as described for benzene, with minor variations in recrystallization and chromatographic techniques. The identity of the various samples of IX, X, and XI with each other was established by mixture melting point, ir, nmr, and tlc retention. The results are recorded in Table III.

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Registry No.—I, 15764-89-3; II, 39974-78-2; III, 50640-05-6; IV, 50640-06-7; VI, 50640-07-8; VII, 50640-08-9; IX, 50640-09-0; X, 50640-10-3; XI, 50640-11-4; 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde hydrazone, 15764-92-8; bromobenzene, 108-86-1; 1,4-diphenyl-1,2,3-triazole-5-carbonitrile, 15764-95-1; 5-aminobenzyl-1,4-diphenyl-1,2,3-triazole, 50640-12-5; 3-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene, 50640-13-6; 2-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene, 50640-14-7; 1-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene, 50640-15-8; 3-methoxy-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene, 50640-16-9; 2-methoxy-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene, 50640-17-0; 1-methoxy-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene, 50640-18-1; *x*-isopropoxy-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene, 50790-96-0; 3-fluoro-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene, 50640-19-2; 2-fluoro-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene, 50640-20-5; 1-fluoro-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene, 50640-21-6; 1,4-diphenyl-5-(α-hydroxybenzyl)-1,2,3-triazole, 50640-22-7.

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Intermediates in Nucleophilic Aromatic Substitution. XII.[1] Kinetic and Equilibrium Study of the Spiro Meisenheimer Complex of 1-(β-Hydroxyethoxy)-2,4-dinitrobenzene

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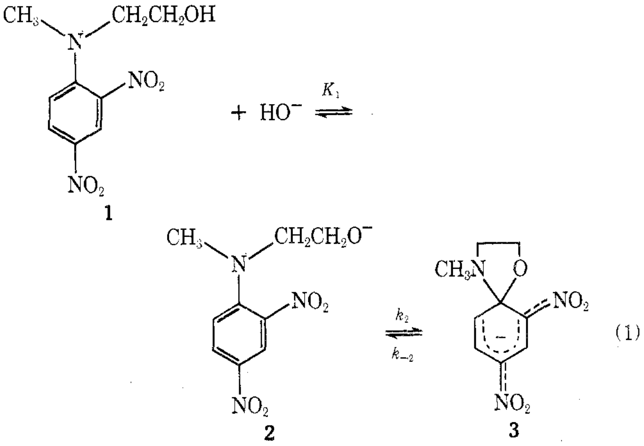
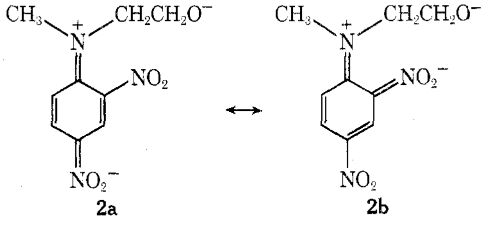
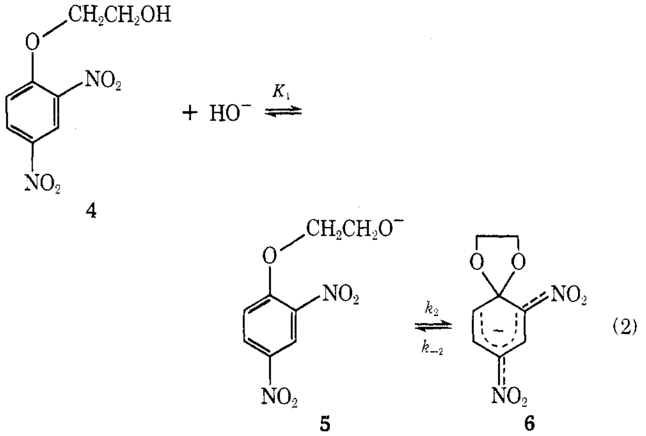
The spiro Meisenheimer complex formed from 1-(β-hydroxyethoxy)-2,4-dinitrobenzene (**4**) in the presence of strong base in aqueous DMSO is considerably more stable than the analogous complex from *N*-β-hydroxyethyl-*N*-methyl-2,4-dinitroaniline (**1**). This difference in stabilities, which becomes more pronounced in DMSO-rich mixtures, is attributed mainly to greater ground-state resonance stabilization in **1**. In water-rich mixtures the rates at which the two spiro Meisenheimer complexes revert to starting materials are almost identical, indicating that the higher stability of the complex derived from the title compound is entirely due to a higher rate of formation. This is shown to be consistent with a complex-like transition state. In DMSO-rich solvents the results indicate a shift toward a more reactant-like transition state in agreement with the Hammond postulate.

We recently published a kinetic study on the formation of the cyclic Meisenheimer complex (**3**) derived from *N*-β-hydroxyethyl-*N*-methyl-2,4-dinitroaniline (**1**) in various mixtures of dimethyl sulfoxide (DMSO) and water.[3] We were particularly concerned with the rate coefficient k_{-2} since it provides a point of reference for the expected rates of leaving-group departure in typical nucleophilic aromatic substitution reactions of amines with 1-X-2,4-dinitrobenzene compounds.[4]



In trying to understand better the factors on which leaving group reactivities depend, we have now investigated the reaction of eq 2. One point of special interest is whether resonance stabilization in **2** (**2a**, **2b**) has a major influence on the rate constants k_2 and k_{-2} of eq 1. Inasmuch as resonance stabilization of this type is expected to be less important in **5**, a comparison between the two systems should be revealing.[5]





Results

Upon addition of base to a solution of **4** in aqueous DMSO, **6**[6] is formed according to eq 2; the stability of **6** relative to the starting materials increases with increasing DMSO content, a well-known phenomenon in Meisenheimer complex chemistry[7] as well as in many other nucleophilic additions or substitutions.[8]

Absorption spectra in 54% DMSO (v/v) at various base concentrations are shown in Figure 1. Owing to hydrolysis the solutions were not very stable; the spectra shown represent extrapolations to zero time.

If we assume that at [KOH] $\geq$ 0.5 *M* conversion to **6** is quantitative, one calculates an extinction coefficient of 21,000 at $\lambda_{\max}$ 495 nm. This extinction coefficient is the same as the one determined indirectly (see below) in 50% DMSO (v/v). Spectra taken in 80% DMSO in the presence of tetramethylammonium hydroxide indicate ϵ_6 32,200 at $\lambda_{\max}$ 500 nm; *i.e.*, ϵ_6 is significantly solvent dependent.

Kinetics. The kinetics of the equilibrium formation of **6** were monitored spectrophotometrically in the stopped-flow (SF) or the temperature-jump (TJ) apparatus. In all runs the base was in a large excess over the substrate concentration, assuring pseudo-first-order kinetics throughout. Thus the reciprocal relaxation time is given by eq 3,