Reaction of a Triazolylcarbene with the Xylenes and Mesitylene and the Resulting Norcaradiene-Tropilidene Rearrangements[1a]

C. D. Bedford,[1b] E. M. Bruckmann, and P. A. S. Smith*

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

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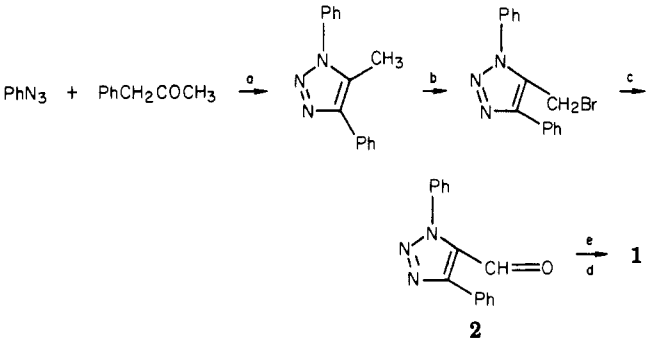
An improved synthesis of 5-(diazomethyl)-1,4-diphenyl-1,2,3-triazole (1) has been developed. It fragments to a carbene at 40–50 °C and reacts with *o*-, *m*-, or *p*-xylene or indan at 40–50 °C to give high yields of cycloheptatriene products, presumably through an initial norcaradiene adduct. In each case only one major isomer was obtained, indicating that steric interactions are a more important influence on the site selectivity of carbene attack than is the electronic directing influence of the alkyl groups. Low-temperature nuclear magnetic resonance spectroscopy found no evidence of dynamic equilibrium between the cycloheptatriene and detectable amounts of the norcaradiene isomers down to −100 °C. With mesitylene, 1 reacted to give an 80% yield of 1,3,5-trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (8), the ^{13}C NMR spectrum of which indicates a dynamic equilibrium with the cycloheptatriene valence tautomer 9. The initial adducts, isolable in their pure state, rearranged on mild heating to isomeric cycloheptatrienes having a structure conjugated with the diphenyltriazolyl substituent. The kinetics were first-order with E_a = 26.9 or 27.9 and 24.8 kcal/mol for the *p*- and *m*-xylene and mesitylene adducts, respectively. The kinetic parameters and the ^1H NMR spectra of the initial adducts and their rearranged isomers are interpretable in terms of the large steric interactions between the diphenyltriazolyl group and the substituents on the cycloheptatriene ring and interference with rotation of the diphenyltriazolyl group but not with conformational inversion. In the rearrangement of 8/9 derived from 2,4,6-trideuteriomesitylene, there was no kinetic isotope effect.

The most general entrance into the norcaradiene–cycloheptatriene system (commonly called tropilidene) is by addition of carbenes to benzene and its derivatives. Although addition of carbenes to aromatic rings was first reported by Büchner and Curtius in 1885[2] and its synthetic utility has been fully explored,[3] much less study has been made of the factors that govern the attack of carbenes on substituted benzenes.

Alder and co-workers[4] reported isomer distribution for the tropilidenes produced in the reaction of photolytically generated (methoxycarbonyl)methylene with a series of substituted benzenes. The data revealed a dominance of steric over electronic effects. However, since the isomer ratios were determined by diene addition to the tropilidenes followed by pyrolysis of the adducts, they probably did not correspond to the kinetically controlled ratios.[5] Subsequently, Müller and co-workers[6] investigated the copper-catalyzed decomposition of diazomethane in substituted benzenes. They found the product distribution to vary somewhat from strictly statistical values, probably due to steric interactions between the ortho substituent and the carbene moiety.

The method of generation of a carbene (or carbenoid species) has been shown to have great influence on its participation in this reaction as well as others. For example, the photolysis of diazomethane in benzene solutions resulted in a 4.8:1 ratio of cycloaddition to insertion products,[3,7] whereas copper-catalyzed decomposition afforded cycloaddition product uncontaminated with insertion product.[6] The factors[8] that have been proposed to account for such differences are spin multiplicity, state of electronic or vibrational excitation, solvation, and coordination or other bonding to metals, and a mechanistic interpretation can be far from unambiguous.[9]

Scheme I[a]



[a] (a) NaOEt, EtOH, 80 °C; (b) *N*-bromosuccimide, Bz_2O_2, CCl_4; (c) Me_2SO, $NaHCO_3$, 80 °C; (d) NH_2NH_2, NEt_3, EtOH; (3) $C_6H_5I(OAc)_2$, cyclohexylamine, CH_2Cl_2, −40 °C.

We have previously reported[10,11] on a carbene source, 5-(diazomethyl)-1,4-diphenyl-1,2,3-triazole (1), which can give less equivocal evidence about the behavior of carbenes because it provides typical carbene reactions on thermolysis at only 40–50 °C without use of a catalyst. Reactions of 1 include ring expansion of benzene and monosubstituted benzenes to cycloheptatrienes cleanly and in high yields. The present study concerns the effects of the position of methyl substituents on the site selectivity for addition of the carbene derived from 1 to the benzene ring and the type of product (noncaradiene or tropilidene) formed (eq 1) by using *o*-xylene, *m*-xylene, *p*-xylene,

(1) (a) Presented in part at the 172nd and 173rd National Meetings of the American Chemical Society, San Francisco, CA, Aug 1976 (Abstract No. ORGN 187), and New Orleans, LA, March 1977 (Abstract No. ORGN 165). (b) From the doctoral Dissertations of C.D.B. and E.M.B.

(2) (a) Büchner, E.; Curtius, T. *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 2877. (b) Büchner, E.; Feldman, L. *Ibid.* **1903**, *36*, 3509. See also the intermediate publications.

(3) (a) Doering, W. v. E.; Knox, L. H. *J. Am. Chem. Soc.* **1950**, *72*, 2305. (b) *Ibid.* **1953**, *75*, 257. (c) Nozoe, T. *Prog. Org. Chem.* **1961**, *5*, 132.

(4) Alder, K.; Muders, R.; Krane, W.; Wirtz, P. *Justus Liebigs Ann. Chem.* **1964**, *675*, 59.

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(7) (a) Meerwein, H.; Disselnkötter, H.; Rappen, F.; von Rintelen, H.; van de Vloed, H. *Justus Liebigs Ann. Chem.* **1957**, *604*, 151. (b) Lemmon, R. N.; Strohmeier, W. *J. Am. Chem. Soc.* **1959**, *81*, 106. (c) Russell, G. A.; Hendry, D. G. *J. Org. Chem.* **1963**, *28*, 1933.

(8) (a) Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042. (b) Schlosser, M.; Heinz, G. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 760; (c) Kirmse, W. "Carbene Chemistry"; Academic Press: New York, 1971; Chapter 10.

(9) Wulfman, D. S.; Poling, B. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York and London, 1980; Vol. 1, Chapter 5.

(10) Smith, P. A. S.; Bruckmann, E. M. *J. Org. Chem.* **1974**, *39*, 1047.

(11) Smith, P. A. S.; Wirth, J. G. *J. Org. Chem.* **1968**, *33*, 1145.

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Table I. ^{1}H NMR Assignments[a] for Tropilidene Adducts from Decomposition of 1 in Xylenes and Mesitylene

position[b]	chemical shift, δ (J, Hz); substituent				
	3	4	6	7	9 (8)
1	4.61 (dd, J_1 = 5.5, $J_{1,2}$ = 9); H	4.37 (m);[c] H	1.81 (s); CH_3	5.17-5.31 (dd, $J_{1,2}$ = 9, $J_{1,7}$ = 5); H	1.40 (s, 3 H); CH_3
2	5.81 (d, $J_{2,1}$ = 9); H	1.75 (s); CH_3	5.88 (d, $J_{2,3}$ = 6); H	6.18 (d, $J_{2,1}$ = 9); H	5.37 (s); H
3	1.82 (s); CH_3	6.13 (s); H	6.05 (d, $J_{3,2}$ = 6); H	2.65 (t); CH_2	1.50 (s); CH_3
4	1.82 (s); CH_3	1.93 (s); CH_3	1.86 (s); CH_3	1.7-2.0 (m); CH_2	5.25 (s); H
5	5.81 (d, $J_{5,6}$ = 9); H	5.80 (d, $J_{5,6}$ = 8.5); H	5.64 (d, $J_{5,6}$ = 9); H	6.18 (d, $J_{5,6}$ = 9); H	1.69 (s); CH_3
6	4.61 (dd, $J_{6,5}$ = 9, $J_{6,7}$ = 5.5); H	4.67 (m);[c] H	4.81 (dd, $J_{6,5}$ = 9, $J_{6,7}$ = 6); H	5.17-5.31 (dd, $J_{6,7}$ = 6, $J_{6,5}$ = 9); H	2.88 (d, J = 6.5); H
7	2.82 (t, $J_{7,6}$ = 5, $J_{7,1}$ = 5.5); H	2.96 (t, $J_{7,6}$ = $J_{7,1}$ = 5.5); H	3.17 (d, $J_{7,6}$ = 6); H	3.31 (t, $J_{7,1}$ = $J_{7,6}$ = 5); H	3.71 (d, J = 6.5); H

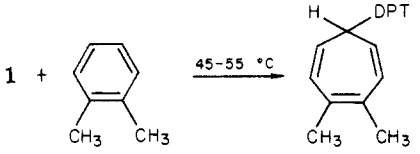
[a] In $CDCl_3$ in parts per million relative to tetramethylsilane. All compounds showed the 7-DPT group at δ 7.7-7.8 (m, 2 H) and 7.4-7.5 (m, 8 H). [b] On the basis of 1,3,5-cycloheptatriene. [c] Not sufficiently well resolved to permit accurate estimation of the coupling constants.

mesitylene, and indan as substrates.

Results and Discussion

Reaction with Arenes. Existing preparative routes to 1 were lengthy and provided poor overall yields. A new synthesis was therefore developed. The original preparation[11] by the Bamford–Stevens reaction of the tosylhydrazone of 1,4-diphenyl-1,2,3-triazole-5-carbaldehyde (2) was cumbersome and only erratically reproducible. It has been prepared in better yield (50%) by oxidation of the unsubstituted hydrazone of 2 with *I,I*-diacetoxyiodobenzene (phenyliodoso acetate).[10] A totally new route[12] to 2 involving oxidation of 5-(bromomethyl)-1,4-diphenyl-1,2,3-triazole by dimethyl sulfoxide proved superior to all literature preparations and consistently gave overall yields of 35% or better by starting from phenyl azide[13,14] and phenylacetone (Scheme I).

Decomposition of 1 in *o*-xylene gave a 73% yield of a single adduct, 3,4-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (3), identified by its ^{1}H NMR spectrum (Table I), which was consistent only with such a symmetrical structure (eq 1).



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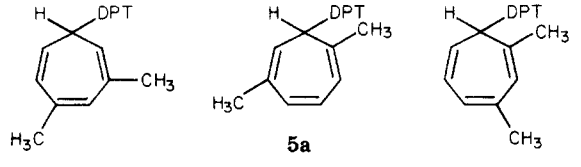
Thermal decomposition of 1 in *m*-xylene afforded a crystalline material in 55% yield; the structure is inferred to be 2,4-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene (4) on the basis of the ^{1}H NMR spectrum

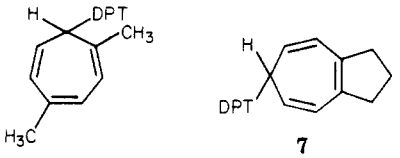


4 5a 5b

(Table I). From the mother liquors from crystallization of 4 was obtained a minor amount of an inseparable mixture that gave an ^{1}H NMR spectrum consistent with a ca. 3:2 ratio of two other tropilidenes, **5a** and **5b**.

When 1 was either thermolyzed or photolyzed in *p*-xylene, a single tropilidene was isolated (ca. 75% yield). On the basis of the ^{1}H NMR spectrum, it was identified as 1,4-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (6).

Indan proved to be a very reluctant reaction partner for 1. The product mixture contained many components, from which only one, 3,4-trimethylene-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (7), could be isolated, in 15%



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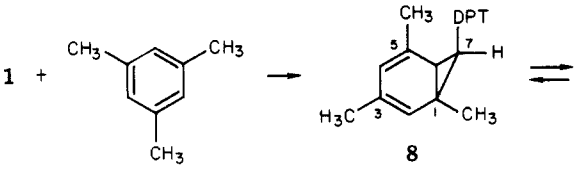
yield. The assigned structure is based on the ^{1}H NMR spectrum (Table I). As with tropilidene 3, only a product with pronounced symmetry is consistent with the NMR spectrum.

Mesitylene reacted with 1 to give a single product in yields greater than 70%. In contrast to the products obtained from the xylenes, spectroscopic data more closely resemble the structure 1,3,5-trimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (8) than the isomeric cycloheptatriene (9) (eq 2).



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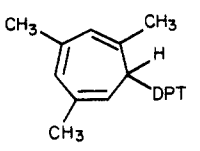

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The ^{1}H NMR spectrum indicated that the product was not the simple nonconjugated tropilidene 9, which might have been expected in analogy to the adducts obtained from monosubstituted benzenes.[10] No C–H insertion products were detected. There were only two one-proton singlets in the vinylic region, at δ 5.73 and 5.26. The presence of the 1,4-diphenyl-1,2,3-triazolyl group was es-

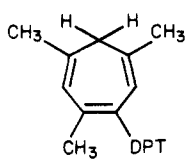
(12) Sheehan, J. C.; Robinson, C. A. *J. Am. Chem. Soc.* **1951**, *73*, 1207.
(13) Alternatively, the aldehyde 2 could be obtained by Raney nickel reduction of 1,4-diphenyl-1,2,3-triazole-5-carbonitrile, on the basis of a method by Staskun and Backeberg for the reduction of hindered nitriles to aldehydes: Staskun, B.; Backeberg, O. G. *J. Chem. Soc.* **1964**, *Suppl. No. 1*, 5880.
(14) Lindsey, R. O.; Allen, C. F. H. "Organic Syntheses"; Wiley: New York, 1951; Collect. Vol. 3, p 710.

Table II. ^{13}C NMR Spectra[a] of 8 (9) and Its Rearrangement Product, 10

compd 8			compd 10		
	shift	mult[c]		shift	mult[c]
CH_3-1	21.9	q	CH_3-1	24.8	q
CH_3-3	23.5	q	CH_3-4	21.0	q
CH_3-5	22.9	q	CH_3-6	24.3	q
C-7	26.2	d	C-7	39.1	t
C-6	81.3	d	vinylic (C-1 to C-6) and		
C-1	88.8	s	aromatic carbons		
vinylic (C-2 to C-5) and aromatic carbons 123.5–146.4[b]			122.5–140.1[b]		

[a] Chemical shifts in parts per million relative to Me_4Si. [b] Due to the complexity of the vinyl and aromatic region, individual assignments were impossible. [c] Multiplicity.

tablished by the characteristic two multiplets in the aromatic region at 7.83 and 7.40 ppm with relative areas of 1:4. The three methyl groups were indicated by three singlets at 1.69, 1.50, and 1.40 ppm. The two remaining protons appeared as doublets (J = 6.5 Hz) at 3.71 and 2.88 ppm. The possibility that the product was a rearranged tropilidene was rejected on the basis of the following considerations. Of the 13 tropilidenes accessible from **9** by 1,5-shifts of hydrogen or the triazole system, only three have two allylic protons: structures **10–12**. Although the



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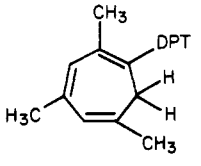

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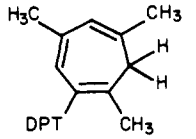

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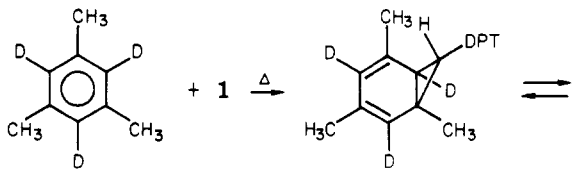
two 7-hydrogens could become magnetically nonequivalent if the diphenyltriazole group is unable to rotate, resulting in syn and anti relationships to the *N*-phenyl and *C*-phenyl groups, the observed chemical shift difference of 0.83 ppm is too great to be accounted for in such a way. Such a difference is reasonable, however, for the 6- and 7-hydrogens of norcaradiene **8**, the immediate product expected from addition of the carbene to the mesitylene nucleus.

Conclusive evidence for the presence of a norcaradiene structure was obtained from the ^{13}C NMR spectrum (Table II). Assignments were made on the basis of relative signal intensities and with the aid of coupled spectra. All cycloheptatrienes possess only four saturated aliphatic carbon atoms. The ^{13}C NMR spectrum indicated six saturated aliphatic carbon atoms to be present. However, the chemical shifts observed for the C-1 and C-6 atoms, 88.7 and 81.3 ppm, respectively, are unusually large and are not convincingly explainable by distortions of the cyclopropane ring system. They are consistent with a dynamic equilibrium between the norcaradiene **8** and its valence tautomer, **9** (eq 2), such as has been established for many related norcaradienes not having hydrogen atoms at the 6- and 7-positions;[15] the ^{13}C NMR shifts are comparable.

Additional structural evidence was obtained by decomposition of **1** in 2,4,6-trideuteriomesitylene (eq 3). The 7-hydrogen resulting from the carbene moiety appeared as a singlet at δ 2.88. The similarity between the coupling constant, $J_{6,7}$ = 5.2 Hz, for 2,5,7-triphenylnorcaradiene (**15**), the only known simple norcaradiene possessing hydrogen atoms at the 6- and 7-positions,[16] and $J_{6,7}$ = 6.5 Hz for **8/9**,



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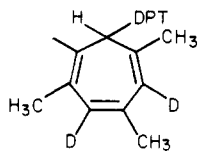

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coupled with the agreement between the chemical shifts of the 1- and 6-hydrogens of known norcaradienes,[17] added further support.

Variable-temperature ^1H NMR investigation of **8/9** showed coalescence of the 6- and 2-hydrogens at −75 to −80 °C into a broad lump. Identification of the two isomeric components was impossible because of the temperature limitation of our instrument and substantial line broadening observed at lower temperatures. Low-temperature ^{13}C NMR investigations, however, also revealed a coalescence temperature of −75 to −85 °C. At −100 °C, the aliphatic region developed new signals attributable to distinct tropilidene components (**8** and **9**). The relative intensities of the new absorptions indicated that the isomer ratio was approximately 1:1. Although explicit assignment of all signals was not possible, the presence of both isomers was clearly indicated. A ratio of ca. 1:1 implies $\Delta G^\circ = 0 \pm 100$ cal/mol between the norcaradiene and tropilidene isomers. This result is consistent with the observation of Hall and Roberts[17a] on 7-aryl-7-carbomethoxy systems and with the value of 40 cal/mol for ΔG° in favor of the cycloheptatriene estimated from equilibrium constants determined at higher temperatures.[18]

Mesitylene has been used as a substrate for a number of carbene species. The copper-catalyzed thermal decomposition of diazomethane in mesitylene yielded only cycloheptatrienes.[6] In the product from (carboethoxy)methylene, a dynamic equilibrium probably exists between norcaradiene and cycloheptatriene, strongly favoring the latter.[19] We have examined the thermal decomposition of phenyldiazomethane and 2-(diazomethyl)-3-phenylthiophene in mesitylene; both compounds appeared to form cycloheptatrienes, as indicated by NMR and mass spectrometric data,[20] but the products were obtained in

(15) Günther, H.; Peters, W.; Wehner, R. *Chem. Ber.* **1973**, *106*, 3683.
(16) Mukai, T.; Kubota, H.; Toda, T. *Tetrahedron Lett.* **1967**, 3581.

(17) (a) Hall, G. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 2203. (b) Ciganek, E. *Ibid.* **1967**, *89*, 1454. (c) Reich, H. J.; Ciganek, E.; Roberts, J. D. *Ibid.* **1970**, *92*, 5166.

(18) The equilibrium constants (K) can be calculated from the ^1H NMR spectra by using the equation $K(\delta_t - \delta_a)/(\delta_a - \delta_n)$, where δ_t, δ_n, and δ_a are the values of δ (H-1,H-6) in tropilidene, norcaradiene, and the equilibrium mixture, respectively. This subject will be elaborated in a following paper.

(19) (a) Büchner, E.; Schottenhammer, D. *Ber. Dtsch. Chem. Ges.* **1920**, *53*, 865. (b) Alder, K.; Munders, R.; Krane, W.; Wirtz, P. *Justus Liebigs Ann. Chem.* **1959**, *627*, 59.

(20) A substance presumed to be 1,3,5-trimethyl-7-phenylcycloheptatriene was isolated from the thermal decomposition of the tosylhydrazone of benzaldehyde in mesitylene in low yield: NMR ($CDCl_3$) δ 1.69 (s, 3 H, CH_3), 1.92 (s, 3 H, CH_3), 2.02 (s, 3 H, CH_3), 3.24 (d, 1 H, CH, J = 7 Hz), 5.43 (d, 1 H, =CH, J = 7 Hz); 5.90 (s, 1 H, =CH), 6.24 (s, 1 H, =CH), 7.25 ppm (s, 5 H, C_6H_5); mass spectrum, m/e 210. From the thermal decomposition of 2-(diazomethyl)-3-phenylthiophene in mesitylene was isolated a substance which appeared to be 1,3,5-trimethyl-7-(3-phenylthien-2-yl)cycloheptatriene in low yield: NMR ($CDCl_3$) δ 1.82 (s, 3 H, CH_3), 1.99 (s, 6 H, CH_3), 3.43 (d, 1 H, CH, J = 7 Hz), 5.37 (d, 1 H, CH, J = 7 Hz), 5.88 (s, 1 H, =CH), 6.18 (s, 1 H, =CH), 7.20 (m, 7 H, aromatic); mass spectrum, m/e 292. The small amounts obtained made purification and further characterization impractical.

low yield and were not isolated in analytically pure form. Other carbene sources result in C–H insertion on the aromatic nucleus.[21] To our knowledge **1** is the only carbene precursor which upon thermolysis in mesitylene has afforded principally a norcaradiene product.

Low-temperature ^{1}H NMR investigations of tropilidenes **3**, **4**, and **6** showed no coalescence, line broadening, or other changes in their respective spectra down to −100 °C. The norcaradiene/cycloheptatriene equilibrium so strongly favors the latter isomers in the xylene adducts[18] that the amount of norcaradiene is below NMR detection levels.

The norcaradiene/cycloheptatriene equilibrium has been an object of more general interest.[22,23] Efforts have been extended toward the preparation of stable substituted norcaradienes, but only a handful of these have met with success, for the equilibrium generally favors the cycloheptatriene. However, bridging the C-1 and C-6 positions with a three-atom bridge,[24] incorporation of one of the double bonds into a condensed aromatic system,[25] or the introduction of strongly negative groups at the C-7 position[26] favors the norcaradiene isomer.

Although these factors may be the most decisive controls on the relative stability of a norcaradiene, the isolation of a norcaradiene **8** from the decomposition of **1** in mesitylene and cycloheptatrienes **4** and **6** from *m*- and *p*-xylene, respectively, emphasize that the balance between these valence tautomers is delicately determined. Whereas tropilidenes **4** and **6** exist wholly as such, the addition of just one methyl group at a position either remote to or on the crucial C-1,C-7,C-6 segment effects a transition to a large equilibrium norcaradiene concentration. These observations may be accounted for if nonbonded interactions between the DPT group and the alkyl substituents differ between the mesitylene adduct and those from the xylenes by ca. 3 kcal/mol.

Because of increased steric interactions between the DPT group and the methyl substituents in **9**, a factor which is only of minor importance in the adducts derived from decomposition of **1** in monosubstituted benzenes, the relative ground-state free energy of **9** evidently approaches or surpasses that of the norcaradiene **8**. These interactions result in an equilibrium where it is now possible for steric strain to be reduced by adopting the norcaradiene structure, thus easing nonbonded interactions of the large DPT group with the methyl substituents and the C-3,4 bridge. In addition, an increase in the relative ground-state free energy of **9b**, the conformer with equatorial DPT, because of steric interactions between the 1-methyl substituent and the DPT group, would favor a shift of the equilibrium toward **9a** and **8a**. Although an equilibrium between **9a** and **9b** would still exist, the equilibrium concentration of **9b** would be small and, in fact, is not observable by NMR techniques. Heyd and Cupas[27] have already demonstrated that a *tert*-butyl group prefers an axial environment in 7-*tert*-butyl-1-methylcycloheptatriene, as a result of large nonbonded interaction with the 1-methyl group, even though the effect is not great enough to promote appreciable equilibration with the norcaradiene valence tautomer.

With respect to selectivity of site of attack, earlier work on the generation of (1,4-diphenyl-1,2,3-triazol-5-yl)methylene in monosubstituted benzenes indicated that electronic factors overshadowed steric interactions between carbene and substrate molecules during the cycloaddition reactions.[10,11] This effect was also demonstrated for the copper-catalyzed decomposition of diazomethane in aromatic substrates.[6] The decomposition of **1** in disubstituted benzenes (i.e., xylenes) also afforded high yields of substituted tropilidenes; however, unlike the monosubstituted benzenes, which afford all three positional isomers in approximately statistical proportions, the disubstituted substrates generally formed only one positional isomer in major amounts, accompanied by only minor quantities of the others.

Examination of the major isomers obtained from the xylenes and mesitylene demonstrates that electronic effects on the aromatic nucleus no longer alone determine the course of carbene cycloaddition. A combination of electronic effects and steric interactions between the alkyl substituents and the attacking carbene affects both the site selectivity of the carbene attack and the type of product (tropilidene or norcaradiene).

Clear evidence of the influence of steric interactions on site selectivity appeared in the *o*- and *m*-xylene cases. The highest electron density in both systems is either next to or between the alkyl substituents. However, the attacking site of the carbene has been altered by nonbonded interactions between the alkyl substituents and the DPT moiety. At least 73% of tropilidene **3** and 55% of tropilidene **4** isolated from *o*- and *m*-xylene arose from attack at a bond at a para position. The product from decomposition of **1** in indan also conforms to this pattern. Although these results indicate that the site selectivity of this carbene attack is markedly influenced by steric interactions, electronic factors may still influence it, directing the electrophilic carbene toward the 3,4- rather than the 2,3-position. In fact, the results from decomposition of **1** in *p*-xylene show that electronic factors still play a major role in carbene site selectivity, for the only product isolated, tropilidene **6**, resulted from carbene attack at the 1,2-bond of the aromatic ring. It is worthy of note that in no case was there detectable evidence for insertion of the carbene from **1** into a C–H bond, even in mesitylene, which confronts the carbene with a crowded ring and nine benzylic hydrogens.

Isomerization of Adducts. An unexpected feature was encountered during purification of **8** (**9**); it was isolable in a pure state but rearranged upon warming (ca. 80 °C) to an isomeric compound, the spectra of which corresponded to 1,4,6-trimethyl-3-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene **10**. This compound (as well as **8** (**9**)) differed qualitatively in ^{1}H NMR spectrum from the products previously obtained from monosubstituted benzenes: in addition to the two diagnostic multiplets for the ten aromatic protons of the DPT group, **10** displayed a broad two-proton singlet at δ 5.77, an AB quartet centered at δ 2.23 (J = 10 Hz, 2 H), and three methyl singlets at δ 1.96, 1.87 and 1.60. The chemical shift of the AB quartet requires that both protons be attached to a saturated carbon, of which only one exists in cycloheptatriene systems.

The ^{13}C NMR spectrum (Table II) of this rearranged material showed only four saturated carbon atoms, three of which were accounted for by the methyl groups. The coupled spectrum showed a triplet for the remaining saturated carbon atom, which can only be interpreted as

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(25) (a) Huisgen, R.; Juppe, G. *Chem. Ber.* **1961**, *94*, 2332. (b) Müller, E.; Kessler, H.; Suhr, H. *Tetrahedron Lett.* **1965**, 423. (c) Nozaki, H.; Yamabe, M.; Noyori, R. *Tetrahedron* **1965**, *21*, 1657.
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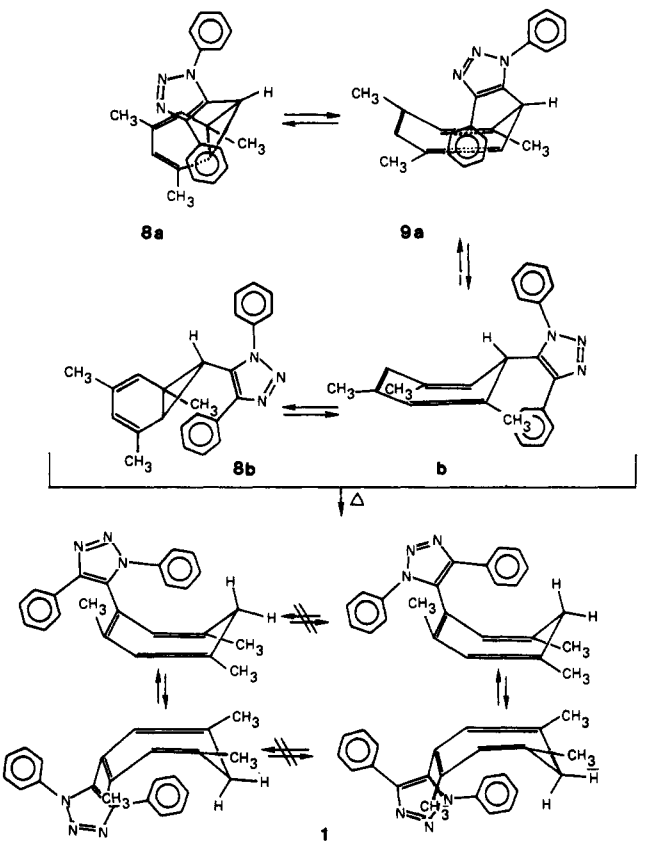
Scheme II



a methylene group. A Cope rearrangement to the nonconjugated tropilidene **9**, followed by an irreversible 1,5 hydrogen shift or a direct 1,5 hydrogen shift with concerted cyclopropane ring opening, would result in the formation of the conjugated tropilidene **10**.

Structure **10** agrees with the ^{13}C NMR spectrum, but the AB quartet present in the ^{1}H NMR spectrum for the methylene group must be explained before the identification can be accepted. It is conceivable that the proximity of the methyl group vicinal to the DPT group could retard the otherwise rapid equilibrium between the two nonplanar boat conformations[28] of **10**. This circumstance would account for the chemical nonequivalence of the methylene hydrogens. However, models indicate that this is not likely. On the other hand, if the large DPT group cannot freely rotate past the vicinal methyl group, as models demonstrate, then two frozen conformations are possible, as in the cases of ortho-tetrasubstituted biphenyls.[29] Without free rotation, the methylene hydrogens are perturbed by either the *N*-phenyl or the *C*-phenyl group, depending on whether they are in a syn or anti orientation. With rapid equilibration of the two nonplanar conformers of **10**, two pairs of enantiomers are generated, in which roughly half of the methylene hydrogens are continually perturbed by the *N*-phenyl group and the other half by the *C*-phenyl group (Scheme II). This results in their chemical nonequivalence and accounts for the AB quartet observed in the NMR spectra.[30] Even at 160 °C, the ^{1}H NMR spectrum of **10** retains the AB quartet, indicating

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(30) A demonstration of the steric interactions between the DPT moiety and vicinal substituents and their subsequent effect on the spectral behavior of the tropilidene adducts is presented in a future paper.

Table III. Kinetics of Rearrangement of 8 (9) and 13 (14) to the Conjugated Tropilidene Isomers

temp, °C	10^5K, s^{-1}	deviation, %
Compound 8 (9)		
89.0	1.50	4.0
100.0	4.11	3.1
107.0	6.65	1.5
110.6	9.78	4.2
118.0	12.5	2.1
129.5	52.8	4.8
138.0	95.2	2.4
Compound 13 (14)		
100.0	4.17	1.9
107.0	7.51	3.1
111.5	11.4	1.6
117.0	17.4	3.1
130.0	47.1	0.7

Table IV. Activation Parameters[a] for the Thermal Isomerization of Mesitylene Adduct 8 (9) and Its Trideuterio Analogue 13 (14)

	8 (9)	13 (14)
E_a, kcal/mol	24.8, 0.7	24.5, 0.4
$\Delta H^{\ddagger}$, kcal/mol	24.0	23.8
$\Delta S^{\ddagger}$, eu	−14.8	−15.4
log A	10.1	10.0

[a] Calculations were made from a mean temperature, 110 °C.

the high barrier to rotation of the DPT group. Assignment of **10** as the structure of the sole isolated rearranged compound from norcaradiene **8** is thus in agreement with all features of the spectra.

The kinetics for the thermal rearrangement of **8** (**9**) to **10** were studied spectrophotometrically. The valence isomerization can be envisioned as occurring by two routes,[16] the most probable of which involves an initial reversible isomerization to the tropilidene **9**, followed by an irreversible 1,5 hydrogen shift to the isolated product **10**. An alternative route[16] proceeds directly to **10** via a concerted 1,5 hydrogen shift. The kinetic data (Tables III and IV) were obtained by measuring areas of the methyl signals of **8** (**9**) and **10** in their ^{1}H NMR spectra. The reaction was first-order in **8** (**9**) with E_a = 24.7 ± 0.7 kcal/mol. Most reported 1,5 hydrogen shifts have an E_a of approximately 30 kcal/mol,[30] with a minimum value of 26 kcal/mol observed[16] for the isomerization of **15**. The energy differences between reported 1,5 hydrogen shifts and that observed for the thermal rearrangement of **8** (**9**) to **10**, 3–5 kcal/mol, supports the postulation of an increased ground-state free energy for **8** (**9**), consistent with the foregoing discussion of the reasons for the norcaradiene structure in the initial product formed from **1** and mesitylene.

Heyd and Cupas[27] reported an activation energy of 19.5 kcal/mol for ring inversion (compared to 6 kcal/mol for cycloheptatriene) between the conformers of 7-*tert*-butyl-1-methycycloheptatriene. The interaction between the DPT group of **8** and the 1-methyl substituent would thus be expected to increase the energy required for interconversion with **9**. The substantial effects of the DPT group on the spectroscopic behavior of tropilidene **10** confirm this postulation. Extrapolating from the 7-*tert*-butyl-1-methylcycloheptatriene system, one concludes that the activation energy for ring inversion of **9a** to **9b** is substantially greater than 20 kcal/mol. We therefore cannot say whether the rate-limiting step is ring inversion of nonpolar tropilidene conformers or the 1,5-shift of a hydrogen affected by the prior equilibrium of conformers.

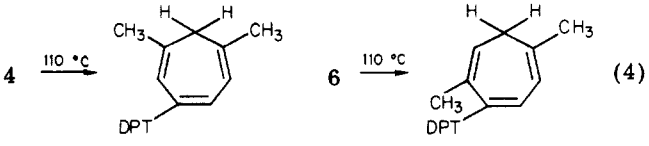
Table V. Kinetics of the Thermal Rearrangement[a] of 4 to 15

temp, °C	10^5K, s^{-1}	deviation, %
108.0	2.31	9.5
111.0	3.08	2.9
118.5	7.93	2.2
129.0	20.0	3.9
138.0	31.3	3.5

[a] Activation parameters (calculated for a mean temperature of 125 °C): E_a = 27.9 ± 1.1 kcal/mol; $\Delta H^{\ddagger}$ = 27.1 kcal/mol; $\Delta S^{\ddagger}$ = −8.8 eu, log A = 11.4 s^{-1}.

The trideuterio analogue of 8 (9), 13 (14), was found to rearrange at the same rate, within experimental error. The absence of a primary isotope effect shows that the ring hydrogens of the original mesitylene are not involved in the rate-limiting stage.

The observation of rearrangement of 8 (9) raised the question of whether the adducts from the xylenes behave similarly. Adducts 4 and 6 were both found to rearrange readily and quantitatively when heated in toluene (3 presumably rearranges also, but there was not enough of it available for further investigation). The products were isomeric tropilidenes, 15 and 16, respectively. The



(4)

15 16

structure of 16 may be assigned on the basis of its NMR spectrum: the two diagnostic multiplets for the ten aromatic hydrogens of the DPT group appeared at δ 7.75 (2 H) and 7.32 (8 H); the three olefinic protons appeared as an AB quartet centered at δ 6.32 and 5.80 ($J_{5,4}$ = 6.0 Hz); a singlet at δ 5.71 and the methylene group appeared as a singlet at δ 2.22; the two methyl groups appeared as singlets at δ 1.95 and 1.83. It is interesting that rearrangement of 4 to 15 afforded only one of two possible isomeric tropilidenes. No product resulting from a 1,5 hydrogen shift to the alkyl-substituted position was detected.

Variable-temperature ^{1}H NMR investigations of 15 showed no alteration of the methylene peak down to −65 °C. Because of the absence of substituents vicinal to the DPT group, no consequences of hindrance to rotation were observed. As a result of this fact and rapid equilibration of the two ring conformations, the methylene group appeared as a singlet.

The kinetics of rearrangement of 4 to 15 were determined by following the disappearance of the methyl signals of 4 in the ^{1}H NMR spectrum; the reaction was first-order in 4, and the numerical data are given in Table V.

Tropilidene 6 also isomerized quantitatively when heated in toluene. Of the two possible isomeric tropilidenes formed by a 1,5 hydrogen shift, only one (16) was isolated. The structure of 16 was assigned on the basis of the NMR spectrum: the three olefinic hydrogens appeared as a pair of doublets at 6.50 and 5.80 ppm ($J_{2,3}$ = 6.0 Hz) and a triplet at 5.18 ppm ($J_{6,7}$ = 7.4 Hz), the methyl groups as two singlets at 1.96 and 1.82 ppm, and the methylene protons as a broad hump centered at 2.22 ppm.

It was evident from the NMR spectrum that only one tropilidene was formed in detectable quantity. The broad hump in the NMR due to the methylene group requires comment, however, for it contrasts with the AB quartet in the NMR spectrum of 10, which resulted from hindered

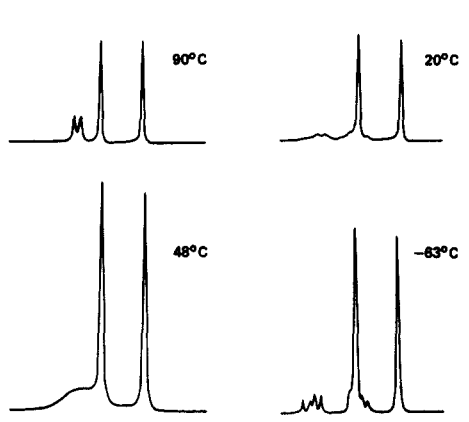


Figure 1. Variable-temperature NMR spectra of tropilidene 16 ($CDCl_3$).

Table VI. Kinetics of the Thermal Rearrangement[a] of 6 to 16

temp, °C	10^5K, s^{-1}	deviation, %
110.7	5.31	2.0
118.5	9.58	4.1
122.0	10.9	5.0
130.0	29.8	1.9
138.0	50.9	0.2

[a] Activation parameters (calculated for a mean temperature of 125 °C): E_a = 26.9 ± 1.1 kcal/mol; $\Delta H^{\ddagger}$ = 26.1 kcal/mol; $\Delta S^{\ddagger}$ = −10.6 eu; log A = 11.0 s^{-1}.

rotation of the DPT group. In the mesitylene case (10), the DPT group and the methyl substituent are attached to the same double bond of the cycloheptatriene, and even at 160 °C, no coalescence of the AB quartet was observed. In 16, however, the vicinal DPT group and methyl substituent are on carbons joined by a single bond, and are thus farther apart. The barrier to rotation of the DPT group past the methyl substituent is therefore lower, and its varying rotational orientation affects the methylene signal.

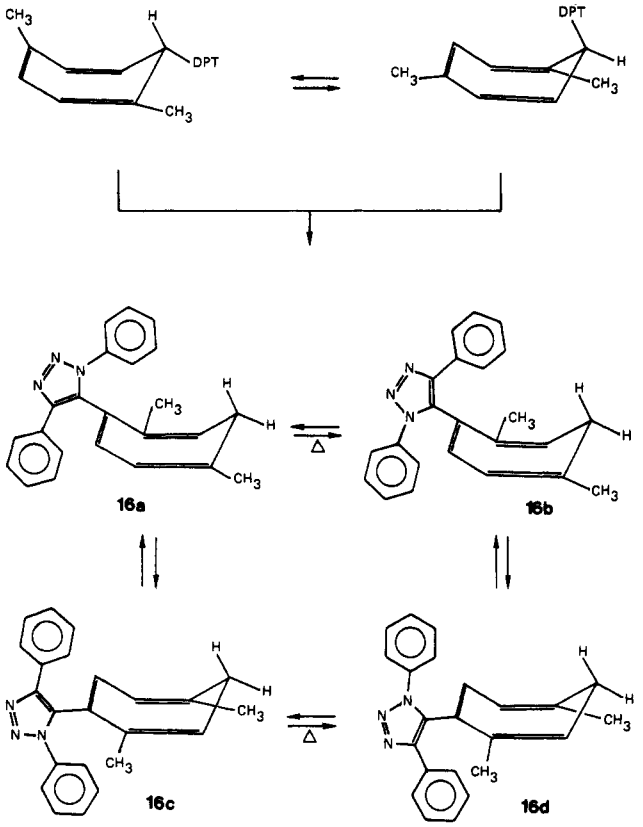
Verification of this analysis was obtained from the NMR spectra of 16 (Figure 1) at other temperatures. At 100 °C, the spectrum of 16 displayed a clean doublet for the methylene protons, centered at δ 2.20 ($J_{7,6}$ = 7.4 Hz), indicating free rotation of the DPT group. However, at −63 °C, 16 displayed a pair of AB quartets, split by the C-6 hydrogen ($J_{7,6}$ = 7.4 Hz), centered at δ 2.48 and 1.94, respectively. As in tropilidene 10, with rapid equilibration of the two nonplanar conformers of 16 and rotation about the triazole–tropilidene bond, two pairs of enantiomers (16a/16d and 16b/16c) are produced such that approximately half of the C-7 hydrogens are constantly perturbed by the *N*-phenyl group and the other half by the *C*-phenyl group (Scheme III). At −63 °C, the C-7 hydrogens are chemically nonequivalent and gave rise to two AB quartets.

The foregoing observations indicate a coalescence temperature of ca. 40 °C for the interconversion of the two rotamers. This corresponds[31] to an activation energy of 17 kcal/mol, with a relative rate (k_1) of 144 s^{-1} for rotation of the DPT group. These observations, like those on tropilidene 10, demonstrate hindrance to rotation of a substituent on a tropilidene ring of considerably greater magnitude than that observed by Heyd and Cupas[27] for the *tert*-butyl group.

The kinetics of thermal rearrangement of 6 to 16, followed by the decrease in area of the methyl signals of 6

(31) Gajewski, J. J. In "Mechanisms of the Molecular Migrations"; Thyagarajan, B. S., Ed.; Wiley: New York, 1971; Vol 4.

Scheme III



in the NMR spectra, were first-order; details are given in Table VI. The values of E_a for rearrangement of **4** and **6** are similar to those reported for other 1,5 hydrogen shifts[30] and not so low as those for the rearrangement of the more crowded **8** (**9**).

The driving force for all three rearrangements is presumably the increase of conjugation reached by having the DPT group attached to an sp^2 carbon and relief of crowding. Evidence for the latter factor is that none of the isomerized tropilidenes equilibrates detectably with its norcaradiene valence tautomer, in contrast to the unisomerized system from mesitylene. The isomerized tropilidenes **10**, **15**, and **16** were unchanged by extended further heating.

Experimental Section[32]

5-(Bromomethyl)-1,4-diphenyl-1,2,3-triazole. In a 500-mL flask were placed 10 g (0.046 mol) of 1,4-diphenyl-5-methyl-1,2,3-triazole,[33] 8.8 g of recrystallized *N*-bromosuccinimide, 2 g of benzoyl peroxide, and 400 mL of carbon tetrachloride. The solution was refluxed for 24 h and was then filtered hot into ca. 1 L of water. The carbon tetrachloride layer was washed with five 500-mL portions of water and was then dried over anhydrous Na_2SO_4; removal of the CCl_4 under aspirator vacuum at room temperature left a reddish, viscous oil, which crystallized on cooling. Recrystallization from absolute ethanol gave 10.8 g (80%) of fine, off-white needles: mp 95–97 °C; NMR ($CDCl_3$) δ 4.48 (s, CH_3), 7.49 (m, 10 H, aromatic).

Anal. Calcd for $C_{15}H_{12}N_3Br$: C, 57.41; H, 3.85; N, 13.37. Found: C, 57.46; H, 3.85; N, 13.33.

1,4-Diphenyl-1,2,3-triazole-5-carbaldehyde (2). To 10 g (0.038 mol) of 5-(bromomethyl)-1,4-diphenyl-1,2,3-triazole and 15 g of anhydrous $NaHCO_3$ was added 100 mL of anhydrous dimethyl sulfoxide under nitrogen gas. The resulting mixture was heated under a positive pressure of nitrogen at 60–100 °C for 45 min to 2 h, and was then poured into 500 mL of ice–water. The crude product mixture (93% material balance based on 100% conversion to aldehyde) was dissolved in a minimal amount of benzene and chromatographed on a column packed with 100–200 g of alumina (100–200 mesh). The column was eluted with benzene and each fraction was examined by TLC after concentration, fractions of similar compositions being combined.

The crude product mixture showed three components by TLC, which were easily separated by column chromatography (elution with benzene). The first fraction amounted to 5.5 g (58.5%) of white needles, mp 169–170 °C. The infrared and NMR spectra were idenical with those of 1,4-diphenyl-1,2,3-triazole-5-carbaldehyde (**2**).[12] The second fraction consisted of 1.3 g (13.8%) of white crystals (mp 184–185 °C) and was identical with 1,4-diphenyl-1,2,3-triazole (IR and NMR spectra identical with those of an authentic sample).[12] This product arises by decarbonylation of **2** under the reaction conditions. Prolonged heating or higher temperatures resulted in the formation of larger amounts of 1,4-diphenyl-1,2,3-triazole. The final fraction, 2.2 g (25%) of yellowish crystals, proved to be 1,4-diphenyl-5-(hydroxymethyl)-1,2,3-triazole, mp 169–170 °C (lit.[34] mp 169–170 °C). Its IR and NMR spectra and TLC behavior were identical with those of the known compound. The overall yield of **2** from 1,4-diphenyl-5-methyl-1,2,3-triazole was 45%.

Reaction of 1 with Arenes. General Procedure. Solutions of 5-(diazomethyl)-1,4-diphenyl-1,2,3-triazole (**1**) ranging in concentration from 0.01 to 0.02 M were prepared[14] in carefully dried equipment by dissolving the diazo compound in the appropriate amount of neat aromatic substrate. The resulting bright red solutions were then flushed with a stream of dry nitrogen for a minimum of 1 h, agitated by magnetic stirring, and then immersed in an oil bath preheated to 45–55 °C. A positive pressure of nitrogen was maintained in the flask throughout the decomposition period. The decompositions were completed after 4 to 5 h, at which time the oil bath was removed and the mixture was allowed to cool to room temperature. The workup procedures are described separately for the individual substrates.

Decomposition in *o*-Xylene. Thermolysis of 522 mg (0.002 mol) of **1** in 70 mL of dry *o*-xylene gave a yellow solution, which was filtered to remove a very small amount of 1,4-diphenyl-1,2,3-triazole-5-carbaldehyde azine.[2] The excess *o*-xylene was removed by vacuum distillation (0.1 mm) at room temperature, leaving a viscous, yellow oil, which was triturated with four 25-mL portions of petroleum ether (bp 30–60 °C). The combined extracts were refrigerated, whereupon 310 mg (46%) of a white, crystalline material precipitated; mp 156–159 °C. The mother liquor was concentrated and chromatographed on 50 g of alumina (activity III). An additional 185 mg (27%) of material, with TLC behavior identical with that of the precipitated compound, was eluted with benzene. On the basis of the NMR spectrum, the adduct was identified as 3,4-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene (**3**). Two recrystallizations from absolute ethanol gave an analytically pure sample: mp 160–161 °C; NMR, see Table I; mass spectrum, *m/e* 339.

Anal. Calcd for $C_{23}H_{21}N_3$: C, 81.29; H, 6.23; N, 12.38. Found: C, 81.29; H, 6.16; N, 12.29.

Decomposition in *m*-Xylene. Thermolysis of 520 mg (0.002 mol) of **1** in 70 mL of freshly distilled reagent grade *m*-xylene gave a brownish yellow solution. A workup procedure identical with that described for the *o*-xylene system yielded 390 mg (55%) of a white solid, mp 169–171 °C. On the basis of the NMR spectrum, the adduct was identified as 2,4-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (**4**). A portion of this material was purified on a 2-mm preparative silicic acid TLC plate by elution with a benzene/ethyl acetate (20:1) mixture. Two crystallizations from absolute ethanol gave an analytically pure sample: mp

(32) All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Varian T-60 and T-60A nuclear magnetic resonance spectrometers were used for ^1H NMR spectra. A JEOL 100-MHz nuclear magnetic resonance spectrometer with Fourier transform capability was used for ^{13}C NMR and variable-temperature spectra. Column chromatography was done on Woelm neutral alumina or silica gel with a fluorescent indicator. Elemental analyses were performed by Spang Microanalytical Laboratory.

(33) Dimroth, O.; Fusoni, E.; Marshall, S. *Ber. Dtsch. Chem. Ges.* **1906**, *47*, 3920.

(34) Senear, A. E.; Wirth, J.; Neville, R. G. *J. Org. Chem.* **1960**, *25*, 807.

171–173 °C; NMR, see Table I; mass spectrum, m/e 339.

Anal. Calcd for $C_{23}H_{21}N_3$: C, 81.36; H, 6.23; N, 12.38. Found: C, 81.22; H, 6.20; N, 12.30.

The mother liquors from isolation of **4** left a small amount of residue, the ^1H NMR spectrum of which corresponded to a 3:2 mixture of **5a** and **5b**: δ 1.51 (s), 1.63 (s), 1.76 (s), 1.84 (s), 4.5–6.2 (m). The mixture did not yield to chromatographic separation.

Decomposition in *p*-Xylene. (a) Thermolysis. Decomposition in the standard fashion of 522 mg (0.002 mol) of **1** in 70 mL of reagent grade *p*-xylene resulted in a yellow solution, from which the excess *p*-xylene was removed by vacuum distillation (0.1 mm) at room temperature. A workup identical with those previously described yielded 450 mg (67%) of a white crystalline material, mp 168–170 °C. The residual material after concentration of the mother liquor consisted of more of the same compound, but less pure. On the basis of the NMR spectrum, it was identified as 1,4-dimethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene (**6**). Recrystallization from absolute ethanol gave an analytical sample: mp 171–173 °C; NMR, see Table I; mass spectrum, m/e 339.

Anal. Calcd for $C_{23}H_{21}N_3$: C, 81.36; H, 6.23; N, 12.38. Found: C, 81.55; H, 6.20; N, 12.14.

(b) Photolysis. A solution of 522 mg of **1** and 50 mL of reagent grade *p*-xylene in a 70-mL test tube was purged with dry nitrogen for 1 h and cooled at 15 °C with an internal cold-finger apparatus. The assembly was placed in a Rayonett photolysis chamber and irradiated with a bank of 3500-Å lights for 5 h. During this time the solution was continually flushed with dry nitrogen, and an internal temperature of 15 °C was maintained. The resulting yellow solution was vacuum distilled (0.1 mm) at room temperature to remove the excess *p*-xylene, and the residual yellow oil was treated in a manner identical with that described for the thermolysis experiments; 485 mg (72%) of tropilidene **6** (mp 170–171 °C; mass spectrum, m/e 339) was obtained.

Decomposition in Indan. Decomposition of 522 mg (0.002 mol) of **1** in 70 mL of freshly distilled indan resulted in a yellow solution, from which the excess indan was removed by vacuum distillation (0.1 mm) at room temperature. The residual oil was triturated with three 25-mL portions of petroleum ether (bp 30–60 °C), and the combined extracts were refrigerated, whereupon 122 mg (17.4%) of a white crystalline material precipitated; mp 157–165 °C. The precipitate was dissolved in a minimal amount of benzene and chromatographed on a column of 25 g of 60–100-mesh Florisil. The column was eluted with a 10:1 mixture of benzene/diethyl ether and each fraction examined by TLC after concentration; fractions of similar composition were combined. Removal of solvent by aspirator distillation afforded 93 mg of white, needlelike crystals of 3,4-trimethylene-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (**7**), mp 169–171 °C. Two recrystallizations from a 1:1 diethyl ether/petroleum ether (bp 30–60 °C) mixture gave an analytically pure sample: mp 170–171 °C; NMR, see Table I; mass spectrum, m/e 351.

Anal. Calcd for $C_{24}H_{21}N_3$: C, 82.02; H, 6.02; N, 11.95. Found: C, 81.98; H, 6.02; N, 11.86.

Decomposition of 1 in Mesitylene. A solution of 0.522 g (0.002 mol) of **1** in 71 mL of reagent grade mesitylene was thermolyzed at 50 °C for 4 h under a positive pressure of nitrogen. The excess mesitylene was removed by vacuum distillation. The oily residue was triturated with three 25-mL portions of petroleum ether (bp 30–60 °C). When the mixture cooled, 0.538 g (80%) of white crystals of **8** (**9**) was obtained: mp 134–173 °C; NMR ($CDCl_3$) δ 7.82 (m, 2 H, aromatic), 7.40 (m, 8 H, aromatic), 5.73 (s, C=CH), 5.25 (s, CH=C), 3.71 (d, J = 6.5 Hz, 1 H), 2.88 (d, J = 6.5 Hz, 1 H), 1.69 (s, CH_3), 1.50 (s, CH_3), 1.40 (s, CH_3). Two cautious recrystallizations from slightly warmed (ca. 35 °C) ethanol gave glossy white leaflets of analytical purity; mp 137–139 °C.

Anal. Calcd for $C_{24}H_{23}N_3$: C, 81.54; H, 6.57; N, 11.90. Found: C, 81.57; H, 6.59; N, 12.02.

A similar experiment using mesitylene with 85% deuterium substitution at the 2-, 4-, and 6-positions prepared by exchange with CF_3CO_2D for 24 h produced an isotopically substituted sample of **8** (**9**) of identical ^1H NMR spectrum except for the near disappearance of the signals at 3.71, 5.25, and 5.73 ppm and the conversion of the doublet at 2.88 ppm to a singlet.

Thermal Rearrangement of 8 (9): 1,4,6-Trimethyl-3-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (10). A solution of 200 mg of **8** (**9**) in 20 mL of absolute ethanol was refluxed overnight. The ethanol was removed under aspirator vacuum, yielding 200 mg of a yellow oil, which crystallized on standing: mp 146–148 °C; NMR ($CDCl_3$) δ 7.95 (m, 2 H, aromatic), 7.40 (m, 8 H, aromatic), 5.77 (br s, 2 H, vinylic), 2.23 (AB q, J = 10 Hz, 2 H, CH_2), 1.96 (s, CH_3), 1.87 (s, CH_3), 1.60 (s, CH_3).

Anal. Calcd for $C_{24}H_{23}N_3$: C, 81.54; H, 6.57; N, 11.90. Found: C, 81.60; H, 6.45; N, 11.99.

Kinetics. The rates of isomerization of the mesitylene and 2,4,6-trideuteriomesitylene adducts were determined in sealed 5-mm NMR tubes which had been washed successively with chromic/sulfuric acid, 10 N sodium hydroxide, distilled water, and acetone and then baked at 100 °C for 24 h. The sealed tube containing 20–50 mg of adduct in ca. 0.5 mL of $CDCl_3$ was placed in a constant-temperature vapor bath. The kinetic data were obtained by measuring the areas of the methyl signals of **8** (**9**) and **13** (**14**) in their NMR spectra at appropriate time intervals after the reaction was quenched by immersion in cold water (see Tables II and III).

Thermal Rearrangement of Tropilidene 6. A solution of 100 mg of compound **6** in 20 mL of reagent grade toluene was refluxed for 24 h. The toluene was removed under aspirator vacuum, leaving 100 mg of a yellow oil, which was chromatographed on a column of 15 g of 60–100-mesh Florisil, developed and eluted with benzene. The only material isolated amounted to 96 mg (96%) of 1,5-dimethyl-4-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (**16**), which crystallized during evaporation of the eluent; mp 138–142 °C. Recrystallization from a 1:1 diethyl ether/petroleum ether (bp 30–60 °C) mixture gave white needles of analytical purity: mp 146–147 °C; NMR ($CDCl_3$) δ 7.86 (m, 2 H, aromatic), 7.40 (m, 8 H, aromatic), 6.50 (d, J = 6.0 Hz, 1 H, C=CCH=C), 5.80 (d, J = 6.0 Hz, 1 H, C=CHC=C), 5.18 (t, J = 7.0 Hz, 1 H, C=CHC), 2.20 (br hump, 2 H, CH_2), 1.96 (s, 3 H, CH_3), 1.552 (s, 3 H, CH_3); mass spectrum, m/e 339.

Anal. Calcd for $C_{23}H_{21}N_3$: C, 81.36; H, 6.23; N, 12.38. Found: C, 81.20; H, 6.61; N, 12.35.

Thermal Rearrangement of Tropilidene 4. A solution of 100 mg of **4** in 20 mL of reagent grade toluene was refluxed for 24 h. The toluene was removed under aspirator vacuum, leaving 100 mg of a yellow oil, which was triturated with two 10-mL portions of petroleum ether (bp 30–60 °C) and cooled, whereupon 89 mg (89%) of a white, crystalline 1,6-dimethyl-3-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (**15**, mp 152–155 °C) precipitated. Recrystallization from a 1:1 diethyl ether/petroleum ether (bp 30–60 °C) mixture gave an analytical sample: mp 158–160 °C; NMR ($CDCl_3$) δ 7.75 (m, 2 H, aromatic), 7.32 (m, 8 H, aromatic), 6.32 (d, J = 6.0 Hz, 1 H, C=CHC=C), 5.80 (d, J = 6.0 Hz, 1 H, C=CCH=C), 5.71 (s, 1 H, C=CHC=C), 2.22 (s, 2 H, CH_2), 1.95 (s, 3 H, CH_3), 1.83 (s, 3 H, CH_3); mass spectrum, m/e 339.

Anal. Calcd for $C_{23}H_{21}N_3$: C, 81.36; H, 6.23; N, 12.38. Found: C, 81.21; H, 6.26; N, 12.42.

Kinetics of Rearrangement of 4 and 6. The thermal isomerizations were conducted as described for rearrangement of **8** (**9**). The results are shown in Tables V and VI.

Registry No. **1**, 15764-89-3; **2**, 75918-79-5; **3**, 75918-80-8; **4**, 75918-81-9; **5a**, 75918-82-0; **5b**, 75918-83-1; **6**, 75918-84-2; **7**, 75918-85-3; **8**, 75918-86-4; **10**, 75918-87-5; **13**, 75918-88-6; **15**, 75918-89-7; **16**, 75918-90-0; 5-(bromomethyl)-1,4-diphenyl-1,2,3-triazole, 75918-91-1; 1,4-diphenyl-5-methyl-1,2,3-triazole, 15765-00-1; 1,4-diphenyl-1,2,3-triazole, 13148-78-2; 1,4-diphenyl-5-(hydroxymethyl)-1,2,3-triazole, 15765-06-7; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; mesitylene, 108-67-8; 2,4,6-trideuteriomesitylene, 38574-14-0.