Table IV. Compositions of Styrene Mixtures and GC Analysis Conditions for Relative Reactivity Studies

reactant	substrate X[a]	O_H/O_X[b]	analysis column	analysis temp, °C
8a	p-CH_3O	1.52	D	130-190
8a	p-CH_3	1.29	D	138
8a	p-Br	0.78	E	160-195
8a	cyclohexene	1.23	C	85-135
22	p-CH_3O	1.52	D	130-190
22	p-CH_3	1.65	D	160
22	p-Br	0.76	E	130
22	cyclohexene	1.49	C	85-125

[a] $XC_6H_4CH=CH_2$ for styrene substrates. [b] Mole ratio for styrene/substrate.

in 6 mL of a 1:1 mixture of cyclohexene and glyme. After 3 h at 0 °C, reaction was found to be only 11% complete by GC analysis. Further reaction at room temperature for 12 h increased the amount of adduct **10a** to 25% of theoretical.

Reaction of Triflate 22 with $PhCH_2NMe_3F$ in Cyclohexene and Glyme. A 5-mL portion of pentane was added under nitrogen to 0.1014 g of a 25% dispersion of powdered $PhCH_2NMe_3F$ (25.4 mg, 0.15 mmol) in mineral oil, and the resulting mixture was stirred for several minutes. The salt was allowed to settle, and then the pentane was removed with a syringe through a serum stopper. This procedure was repeated twice, and then the residual pentane was removed with a stream of N_2. Reaction of triflate **22** (27.6 mg, 0.1 mmol) with this fluoride source was carried out at -20 °C in 3 mL of a 5:1 mixture of glyme and cyclohexene. As before, reaction was found to be complete after 1.5 h of vigorous stirring, and adduct **10a** was found to have formed in 91.7 ± 0.2% yield (from duplicate runs). A reaction set up as above with a 1:1 mixture of cyclohexene and glyme and a reaction temperature of 0 °C gave 79% of adduct **10a**.

Reaction of Triflate 22 with Aqueous KF and Aliquat 336 in Cyclohexene. Triflate **22** (27.6 mg, 0.1 mmol) was reacted at 0 °C in a two-phase system consisting of 58 mg of 50% aqueous KF (29 mg, 0.5 mmol of KF) and a solution of 76 mg (0.15 mmol) of Aliquat 336[39] in 3 mL of cyclohexene. Vigorous and turbulent stirring was maintained during the reaction to achieve good interaction of the two phases. Again, no **22** remained after 1.5 h of reaction. An average yield of 82.1 ± 0.4% was observed for adduct **10a** from duplicate runs. Further analysis of each mixture on column C at 70-100 °C revealed the presence of 2-methyl-1-propenyl triflate (**24**) in 2.3 ± 0.3% yield.

Reaction of Triflate 22 with Aqueous KF and 10% Aliquat 336 in Cyclohexene. The procedure described above was used except that 5.0 mg (0.01 mmol) of Aliquat 336 and room temperature were used for this reaction. After 1 h of vigorous stirring, adduct **10a** had been formed in 8% yield. The yield increased to 11% after 40 h. Addition of 55.5 mg (0.11 mmol) of Aliquat 336 followed by 0.5 h of reaction resulted in the formation of **10a** in 74% yield.

General Procedures for the Selectivity Experiments. The following was used for the reactions of (tosylazo)alkene **8a**. A solution of 0.050 g (0.21 mmol) of **8a** in 1 mL of the appropriate styrene mixture was allowed to stand at 0 °C until reaction was complete, usually about 3 days. Direct analysis of the mixture was then carried out on a gas chromatograph. The results of multiple injections of duplicate runs are listed in Tables II and III. Table IV gives the composition of the styrene mixtures used and the conditions of GC analysis.

For reactions of silylvinyl triflate **22**, a suspension of benzyltrimethylammonium fluoride (25 mg, 0.15 mmol), 0.5 mL of glyme, and 0.5 mL of the appropriate sytrene mixture was cooled to 0 °C, and triflate **22** (24 mg, 0.087 mmol) was added. After vigorous mixing, the solution was allowed to stand for 24 h at 0 °C before direct GC analysis. As for **8a**, results and conditions are given in Tables II-IV.

Acknowledgment. This investigation was supported by the National Cancer Institute (CA 16903-06) of the National Institutes of Health.

Registry No. **8a**, 62618-93-3; **8b**, 42449-08-1; **10a**, 53282-47-6; **10b**, 19690-02-9; **11a**, 87185-17-9; **11b**, 87185-15-7; **12a**, 87189-83-1; **12b**, 87185-14-6; **16**, 87185-16-8; **21**, 56583-93-8; **22**, 73876-87-6; p-$CH_3OC_6H_4CH=CH_2$, 637-69-4; p-$CH_3C_6H_4CH=CH_2$, 622-97-9; $C_6H_5CH=CH_2$, 100-42-5; p-$BrC_6H_4CH=CH_2$, 2039-82-9; $(CH_3)_2C=C:$, 26265-75-8; cyclohexanecarboxaldehyde tosylhydrazone, 34266-29-0; isobutyraldehyde tosylhydrazone, 20208-71-3; 2-(p-bromophenyl)-1-isopropylidenecyclopropane, 87185-13-5.

Site of Attack of a Carbene on Alkylbenzenes, Naphthalene, and Thiophene and the Norcaradiene-Cycloheptatriene Equilibration

Clifford D. Bedford[1] and Peter A. S. Smith*

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

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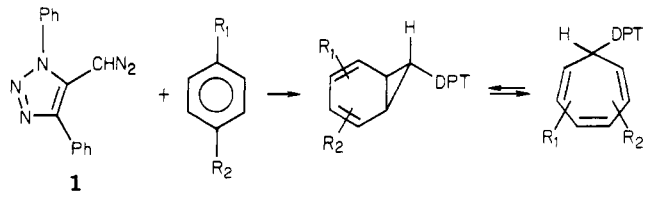
Upon thermolysis at 40-50 °C, 5-(diazomethyl)-1,4-diphenyl-1,2,3-triazole (**1**) reacts with p-ethyltoluene, p-cymene, p-*tert*-butyltoluene, p-diisopropylbenzene, durene, and naphthalene to give a mixture of carbene-derived cycloheptatriene/norcaradiene products; attack is favored adjacent to the more highly branched substituent. Decomposition of **1** in p-diisopropylbenzene afforded a tropilidene and a C-H insertion product in a ca. 1:1 ratio. Naphthalene was attacked at the 1,2-position to form a norcaradiene and at the 2,3-position to form a cycloheptatriene. Thiophene was attacked only at the 2,3-position, with formation of a cyclopropanothiophene. The kinetics of the thermal rearrangement of the product from 4-*tert*-butyltoluene to an isomeric cycloheptatriene were first order; E_a = 24.90 ± 0.4 kcal/mol, and $\Delta S^{\ddagger}$ = 14.5 eu. The NMR spectrum of the isomer showed the presence of rotamers and conformers with high energy barriers between them, such that they are individually recognizable at room temperature.

Introduction

In previous articles[2] we have demonstrated that the position and number of alkyl substituents on an aromatic substrate influence the site selectivity of carbene addition, as well as the structure of the product, norcaradiene (NCD) or cycloheptatriene (CHT). In the present study, the effect of branching and number of the alkyl substituents and of benzo fusion on the structure of the product and site selectivity has been investigated. 5-(Diazomethyl)-1,4-diphenyl-1,2,3-triazole (**1**) affords a favorable opportunity

(1) In part from the doctoral dissertation of C.D.B.
(2) Bedford, C. D.; Bruckmann, E. M.; Smith, P. A. S. *J. Org. Chem.* 1981, *46*, 679.

0022-3263/83/1948-4002$01.50/0

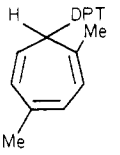


1

$R_1 = R_2$ = alkyl; DPT = 1,4-diphenyl-1,2,3-triazol-5-yl

to investigate these factors, because of the large steric interactions between the diphenyltriazolyl group and the alkyl substituents.

Reaction of the carbene from diazo compound **1** with *p*-xylene gives only one product,[2] **2**, resulting from addition



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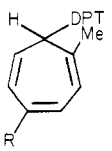
at the 1,2-bond of the *p*-xylene. In view of this selectivity, we undertook a study of the effects of the size of the alkyl substituent on the products obtained from a series of para-substituted benzenes, embracing thermal decomposition of **1** in *p*-ethyltoluene, *p*-cymene, *p*-*tert*-butyltoluene, *p*-diisopropylbenzene, and *p*-di-*tert*-butylbenzene. Durene was investigated for comparison with previous results on the xylenes and mesitylene, and naphthalene and thiophene were included in order to examine the effect of π-electron interactions.

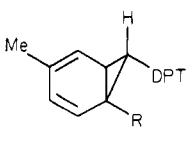
Results and Discussion

Solutions of crystalline **1** in a large excess of a liquid substrate were heated at 45 to 55 °C. When the substrate was a solid, methylene chloride was used as a solvent. In each case, a mixture of isomeric tripilidenes was obtained, from which only one component could generally be isolated by crystallization. For quantitative assay, the mixed isomers were freed from traces of aldazine and other contaminants by column chromatography and were examined by NMR. Structures were elucidated by ^{1}H NMR with the aid of decoupling, supplemented where needed by ^{13}C NMR, and all isomers could be satisfactorily assayed. The diphenyltriazolyl groups in all cases gave rise to a 10 H multiplet in the range δ 7.4–7.8; the other NMR features and their assignments are given in Tables I and II. Attempts at chromatographic separation offered no quantitative improvements. The sites of addition are summarized in Table III.

Site of Attack. Decomposition of **1** in *p*-ethyltoluene gave an inseparable pair of positionally isomeric tropilidenes[3] in a ratio of ca. 1:1. One component corresponded to 1-methyl-4-ethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)-cycloheptatriene (**3a**), and the other consisted of roughly



3a, R = Et
4a, R = *i*-Pr

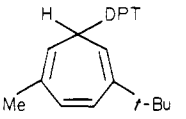


3b, R = Et
4b, R = *i*-Pr
5b, R = *t*-Bu

equal amounts of 1-ethyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (**3b**) and its CHT valence tautomer, 1-ethyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene.

The components from the thermolysis of **1** in *p*-cymene were identified[3] as 1-methyl-4-isopropyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (**4a**) and 1-isopropyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (**4b**), in a ratio of ca. 1:1.3.

When **1** was thermolyzed in *p*-*tert*-butyltoluene, the major product[3] was 1-*tert*-butyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (**5b**) (plus its CHT valence tautomer), inseparable from an isomer (5–15% yield), 2-*tert*-butyl-5-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (**6a**).



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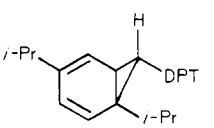
Decomposition of **1** in *p*-diisopropylbenzene afforded a crystalline but inseparable mixture of two isomers, which were identified by NMR as 1,4-diisopropyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (**7**) and 1,4-di-



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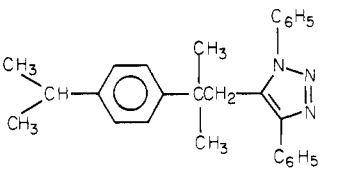
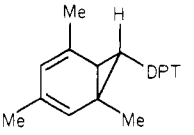


8

phenyl-5-[2-(*p*-isopropylphenyl)-2-methylpropyl]triazole (**8**). Compound **8** is the first example we have detected of C–H insertion by **1** competing with addition to the benzene ring.

The ^{1}H NMR spectrum of the mixture indicated the absence of a CHT isomer (compare the spectrum of **7** with that of NCD **4b**, Table I). Additional evidence for the structure of **7** was obtained from ^{13}C NMR. The C-6 and C-1 carbon atoms appear at δ 65.35 and 65.00, respectively, as a doublet and singlet when coupled. These shifts are siimilar to those for the mesitylene adduct **9** and for NCD's known to be in dynamic equilibrium with their valence isomers.[4]



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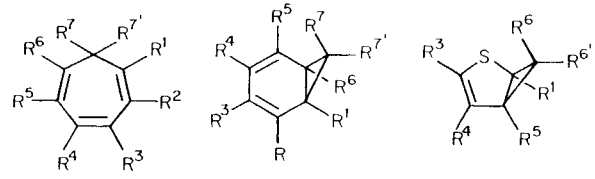
The structure of **8** was deduced as follows. A complex 4 H multiplet at δ 7.0 corresponds to the aryl hydrogens of the *p*-diisopropylbenzene skeleton. The methylene group can be identified with a singlet at δ 3.34, the isopropyl methine hydrogen can be identified with a multiplet at δ 2.80, the isopropyl methyls with a 6 H doublet at δ 1.19, and the interior geminal methyls can be identified with a 6 H singlet at δ 0.92. The methylene carbon atom appears at δ 36.6 as a triplet in the coupled ^{13}C NMR spectrum, confirming the methylene assignment.

Thermolysis of **1** in *p*-di-*tert*-butylbenzene was the only one that failed to yield carbene cycloaddition products. Only 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde and its azine[5] were isolated from the complex mixture produced.

(3) For convenience, substances shown by spectra in solution to be equilibrating systems with a substantial content of norcaradiene are named as norcaradienes; those whose spectra show overwhelmingly cycloheptatriene structure are so named.

(4) Günther, H.; Peters, W.; Wehner, R. *Chem. Ber.* **1973**, *106*, 3683.

Table I. Proton Chemical Shifts for the Initial Adducts Obtained from the Decomposition of 1 in Aromatic Substrates



compd	chemical shifts, δ							
	R^1	R^2	R^3	R^4	R^5	R^6	R^7	$R^{7'}$
2	CH_3, 1.81 (s)	H, 5.88 (d, $J_{2,3}$ = 9.0 Hz)	H, 6.05 (d, $J_{3,2}$ = 9.0 Hz)		H, 5.64 (d, $J_{5,6}$ = 9.0 Hz)	H, 4.81 (dd, $J_{6,5}$ = 9.0 Hz, $J_{6,7}$ = 6.0 Hz)	H, 3.71 (d, $J_{7,6}$ = 6.0 Hz)	DPT, 7.75 (m, 2 H), 7.45 (8 H)
3a	CH_3, 1.71 (s)	H, 5.62 (d, $J_{2,3}$ = 8.0 Hz)	H, 5.90 (d, $J_{3,2}$ = 8.0 Hz)	CH_3CH_2, 2.12 (br q); CH_3CH_2, 0.82 (br t)	H, 5.72 (d, $J_{5,6}$ = 7.0 Hz)	H, 4.75 (dd, $J_{6,5}$ = 7.0 Hz, $J_{6,7}$ = 6.0 Hz)	H, 3.14 (d, $J_{7,6}$ = 6.0 Hz)	DPT, 7.55 (m, 10 H)
4a	CH_3, 1.70 (s)	H, 5.68 (d, $J_{2,3}$ = 8.0 Hz)	H, 6.00 (d, $J_{3,2}$ = 8.0 Hz)	$(CH_3)_2CH$, 2.25 (m); $(CH_3)_2CH$, 0.92 (dd)	H, 5.68 (d, $J_{5,6}$ = 8.0 Hz)	H, 4.63 (m)	H, 3.05 (d, $J_{7,6}$ = 7.0 Hz)	DPT, 7.57 (m, 10 H)
6	H, 5.10 (d, $J_{1,7}$ = 7.0 Hz)	$(CH_3)_3C$, 0.98 (s)	H, 6.61 (d, $J_{3,4}$ = 11.0 Hz)	H, 6.38 (d, $J_{4,3}$ = 11.0 Hz)	CH_3, 1.82 (s)	H, 5.10 (d, $J_{6,7}$ = 7.0 Hz)	H, 3.03 (t, $J_{7,1}$ = $J_{7,6}$ = 7.0 Hz)	DPT, 7.85 (m, 2 H), 7.50 (m, 8 H)
8	CH_3, 1.40 (s)	H, 5.26 (s)	CH_3, 1.50 (s)	H, 5.73 (s)	CH_3, 1.69 (s)	H, 3.71 (d, $J_{6,7}$ = 6.5 Hz)	H, 2.88 (d, $J_{7,6}$ = 6.5 Hz)	DPT, 7.83 (m, 2 H), 7.40 (m, 8 H)
3b C	CH_3CH_2, 2.12 (br q); CH_3CH_2, 0.92 (br t)	H, 5.82 (d, $J_{2,3}$ = 7.0 Hz)	H, 6.05 (d, $J_{3,2}$ = 7.0 Hz)	CH_3, 1.73 (s)	H, 5.40 (d, $J_{5,6}$ = 8.0 Hz)	H, 3.91 (br t, $J_{6,5}$ = 8.0 Hz, $J_{6,7}$ = 7.0 Hz)	H, 2.86 (d, $J_{7,6}$ = 7.0 Hz)	DPT, 7.55 (m, 10 H)
4b	$(CH_3)_2CH$, 1.77 (m); $(CH_3)_2CH$, 0.75 (dd)	H, 5.33 (d, $J_{2,3}$ = 8.4 Hz)	H, 5.77 (d, $J_{3,2}$ = 8.4 Hz)	CH_3, 1.62 (s)	H, 5.12 (d, $J_{5,6}$ = 8.0 Hz)	H, 3.59 (br t, $J_{6,5}$ = 8.0 Hz, $J_{6,7}$ = 6.5 Hz)	H, 3.13 (d, $J_{7,6}$ = 6.5 Hz)	DPT, 7.68 (m, 2 H), 7.45 (m, 8 H)
5a	$(CH_3)_3C$, 0.92 (s)	H, 5.44 (d, $J_{2,3}$ = 8.0 Hz)	H, 6.04 (d, $J_{3,2}$ = 8.0 Hz)	CH_3, 1.54 (s)	H, 5.70 (d, $J_{5,6}$ = 8.5 Hz)	H, 3.74 (br t, $J_{6,5}$ = 8.5 Hz, $J_{6,7}$ = 7.0 Hz)	H, 2.87 (d, $J_{7,6}$ = 7.0 Hz)	DPT, 7.60 (m, 10 H)
10a	CH_3, 1.38 (s)	H, 4.72 (s)	CH_3, 1.46 (s)	CH_3, 1.46 (s)	H, 4.72 (s)	CH_3, 1.38 (s)	H, 2.87 (s)	DPT, 7.51 (m, 10 H)
10b	CH_3, 0.99 (s)	CH_3, 1.36 (s)	H, 5.57 (s)	CH_3, 1.63 (s)	CH_3, 1.30 (s)	H, 2.49 (d, $J_{6,7}$ = 6.0 Hz)	H, 2.10 (d, $J_{7,6}$ = 6.0 Hz)	DPT, 7.80 (m, 2 H), 7.50 (m, 8 H)
11a	H, 2.26 (q)	CH_3=CHCH=CH, 7.06 (m, 4 H)		H, 6.29 (d, $J_{4,5}$ = 9.5 Hz)	H, 5.90 (dd, $J_{5,4}$ = 9.5 Hz, $J_{5,6}$ = 4.7 Hz)	H, 1.75 (m)	H, 1.35 (t)	DPT, 7.83 (m, 2 H), 7.50 (m, 8 H)
11b	H, 4.85 (dd)	H, 5.75 (d)	CH=CHCH=CH, 7.05 (m, 4 H)		H, 5.75 (d)	H, 4.85 (dd)	H, 2.90 (t)	DPT, 7.90 (m, 2 H), 7.40 (m, 8 H)
12	H, 2.70 (dd, $J_{1,6}$ = 3.0 Hz, $J_{1,5}$ = 8.0 Hz)		H, 6.00 (d, $J_{3,4}$ = 6.0 Hz)	H, 5.58 (dd, $J_{4,3}$ = 6.0 Hz, $J_{4,5}$ = 3.0 Hz)	H, 2.34 (m)	H, 1.62 (t, $J_{6,1}$ = $J_{6,5}$ = 3.0 Hz)	6'-DPT, 7.75 (m, 2 H); 7.43 (m, 8 H)	

Table II. ^{13}C NMR Spectra of 1,3,4,6-Tetramethyl-7-(diphenyltriazolyl)norcaradiene (10a) and 1-*tert*-Butyl-4-methyl-7-(diphenyltriazolyl)cycloheptatriene (5b)

compd	position	δ[a]	multiplicity in coupled spectrum
10a	CH_3-1, CH_3-6	19.20	q
	CH_3-3, CH_3-4	22.72	q
	C-7	27.27	d
	C-1, C-6	63.37	s
	alkene and aromatic C's	124.5-147.6	m
5b	CH_3-4	23.08	q
	C-7	27.69	d
	$(CH_3)_3C$-1	34.18	q
	$(CH_3)_3C$-1	34.73	s
	C-6	120.40	d
	alkene and aromatic C's	122.95-147.34	m

[a] Relative to tetramethylsilane.

Table III. Carbene Adducts from 1 and Aromatic Substrates

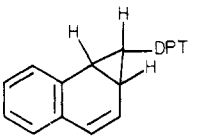
substrate	total yield, %	site of addition	ratio of products
1-CH_3-4-C_2H_5-C_6H_4	68	1,2 (3a), 3,4 (3b)	1:5
1-CH_3-4-*i*-C_3H_7-C_6H_4	87	1,2 (4a), 3,4 (4b)	1:1.3
1-CH_3-4-*t*-C_4H_9-C_6H_4	75	2,3 (6), 3,4 (5b)	1:5-1:15
1,4-(*i*-$C_3H_7)_2$-C_6H_4	80	1,2 (7), α (8)	1:1
1,4-(*t*-$C_4H_9)_2$-C_6H_4	0	none	
1,2,4,5-$(CH_3)_4$-C_6H_2	56	1,2 (10a), 2,3 (10b)	9:1
naphthalene	91	1,2 (11a), 2,3 (11b)	3:2
thiophene	55	2,3 (12) only	>100:1

The overall similarity of the NMR spectra of CHT's **2**, **3a**, **4a**, and **6** (Table I) reinforces the individual assignments of 1-methyl-4-alkyl substitution on the CHT ring. The structures of the NCD's **3b**, **4b**, and **5b** are also supported by the overall similarity of their spectra with that of NCD **9** (Table I) and the chemical shifts of reported NCD's.[6]

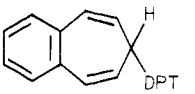
Decomposition of **1** in a durene/dichloromethane solution gave a 56% yield of a solid mixture, from which the major component was separated and identified by ^1H and ^{13}C NMR as 1,3,4,6-tetramethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (**10a**), resulting from attack at the 1,2 edge. A minor adduct (ca. 11%) proved to be the isomeric NCD **10b**, resulting from attack at the 2,3 edge.

Thermolysis of **1** in a naphthalene/dichloromethane solution afforded a 3:2 mixture of 7-(1,4-diphenyl-1,2,3-triazol-5-yl)-2,3-benzonorcaradiene (**11a**) and its isomer, 7-(1,4-diphenyl-1,2,3-triazol-5-yl)-3,4-benzocycloheptatriene (**11b**), separable by chromatography.

When **1** was thermolyzed in thiophene, only a single adduct, 6-(1,4-diphenyl-1,2,3-triazol-5-yl)-2-thiabicyclo-[3.1.0]hex-3-ene (**12**), was isolated, present entirely as the

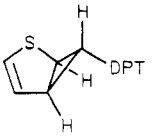


11a



11b

analogue of the norcaradiene structure.



12

The products of the foregoing experiments are taken to be the initial, kinetically determined ones for the purposes of the ensuing discussion. We recognize the possibility in principle of positional isomerization by a ring-walk path but think it improbable because the reaction conditions were very mild (45–55 °C), whereas ring-walk isomerization usually requires 180–300 °C, and even the most exceptionally easy examples, the 7,7-dicyanonorcaradienes, require 75 °C for slow isomerization.[7] The present examples do not have the necessary features for easy isomerization: weakening of the C1–C7 bond by powerfully electron-withdrawing 7-substituents and existence almost entirely as the norcaradience valence tautomer. However, we cannot rigorously exclude ring-walk isomerization, owing to the ease with which 1,5-sigmatropic shift of hydrogen occurs.[2]

Our earlier results[2] did not determine whether the α-substituent (diphenyltriazolyl) was oriented syn or anti to the substrate nucleus in the addition step, owing to the rapid equilibration between the valence tautomers. However, the NMR spectra of **11a** and **12** clearly demonstrate a trans relationship between the erstwhile carbene hydrogen and the bridgehead hydrogens, manifest in the coupling constants observed for the 1,7- and 6,7-hydrogens of **11a**, 4.7 Hz, and the 1,6- and 5,6-hydrogens of **12**, 3.0 Hz. These values fall in the range observed for vicinal trans cyclopropane hydrogens and are far below the lowest observed for cis hydrogens (7 Hz).[8] This indicates that the DPT group has added in an anti manner with respect to the naphthalene or thiophene ring. This conclusion depends on the assumption that the initial adduct does not isomerize and that the product is kinetically determined. This assumption is supported by the fact that these products are single isomers and not evident equilibrium mixtures and that interconversion with a CHT isomer, the path for syn–anti isomerization of a NCD, does not appear to be taking place. The anti selectivity displayed by 1,4-diphenyl-1,2,3-triazol-5-ylmethylene parallels the behavior of ethoxycarbonylmethylene toward the naphthalene nucleus.[9] However, ethoxycarbonylmethylene specifically attacks the 1,2 (or 3,4) edge and does not produce recognizable quantities of products derived from attack at the 2,3 edge, in contrast to our results with **1**. The two situations differ also in the temperature (160 vs. 50 °C).

The diphenyltriazolylmethylene is probably essentially planar and, presumably, descends axially to the benzene

(5) (a) Smith, P. A. S.; Wirth, J. G. *J. Org. Chem.* **1968**, *33*, 1145. (b) Smith, P. A. S.; Bruckmann, E. M. *J. Org. Chem.* **1974**, *39*, 1047.

(6) (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.

(7) Berson, J. A.; Grubb, P. W.; Clark, R. A.; Hartter, D. R.; Wilcott, III, M. R. *J. Am. Chem. Soc.* **1967**, *89*, 4076.

(8) Graham, J. D.; Rogers, M. T. *J. Am. Chem. Soc.* **1962**, *84*, 2249. Chamberlain, N. F. "The Practice of NMR Spectroscopy"; Plenum Press: New York, 1974; pp 99 and 299.

(9) (a) Huisgen, R.; Juppe, G. *Chem. Ber.* **1961**, *94*, 2332. (b) Boekelheide, V.; Smith, C. D. *J. Am. Chem. Soc.* **1966**, *88*, 3950.

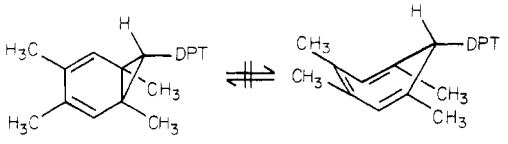
ring, with its plane oriented roughly parallel. The initial process may be formation of a π-complex, which could be transformed into a dipolar σ-complex by localization of bonding at a single carbon of the benzene ring or directly into a NCD by localization of bonding simultaneously to two adjacent carbons.

Even if the triazole system is itself involved in the π-complex, its preferred orientation would be away from the branched substituent, toward which the carbenic carbon would thereby be brought closer. With two branched substituents para to each other, no orientation of a π-complex involving the triazole system would fully avoid steric interference, and attack would be retarded, as observed in the case of *p*-diisopropylbenzene, or prevented, as in the case of *p*-di-*tert*-butylbenzene. In the former instance, this situation is presumably responsible for a change in the site of reaction to the isopropyl tertiary C–H, which is more reactive toward insertion than are primary and secondary C–H.

If in the eventual formation of a tropilidene, such as **5b**/**13**, the DPT group rotates to an anti orientation to the benzene ring, the initial conformation would be as represented by **13a**, with the DPT group exo (equatorial), in agreement with the geometry observed in **11a** and **12**.

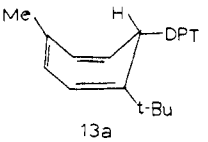
Valence Tautomerism. The (NCD/CHT) equilibrium has been an object of wide interest.[10] Efforts have been extended toward the preparation of stable substituted NCD's, but only a handful of them have met with success, for the equilibrium generally lies on the CHT side. However, bridging the 1- and 6-positions with a three-atom bridge,[11] incorporation of one of the double bonds into a condensed aromatic system,[9,12] or the introduction of strongly electronegative groups at the 7-position[10,13,14] or *tert*-butyl groups at the 2- and 5-positions[15] favors the NCD isomer.

Although these factors may be the most decisive controls on the stability of a NCD, the identification of substantial concentrations of NCD's **9**, **10a**, and **10b** from the decomposition of **1** in mesitylene and durene emphasizes that the balance between valence tautomers may be more subtly determined: the addition of one methyl group to **2** effects a transition from wholly CHT to a large equilibrium NCD concentration, **9**, and the addition of two methyl groups brings about a total transition to the NCD isomers **10a** and **10b**.

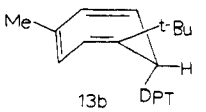


10a **14**

A plausible explanation may be found by considering steric factors. The steric interactions between the 7-DPT substituent and the C-1 and/or C-6 groups favor an axial (endo) geometry in the CHT forms. This postulation is substantiated by the work of Heyd and Cupas,[16] who reported an activation energy of 19.2 kcal/mol for ring inversion of 7-*tert*-butyl-1-methylcycloheptatriene and established that the conformation having the 7-*tert*-butyl group axial (endo) was preferred. Analogously, the even larger interaction between the 7-DPT group and the 1- and/or 6-alkyl groups would cause the energy content of the exo CHT conformer, such as **13a**, to be greater than



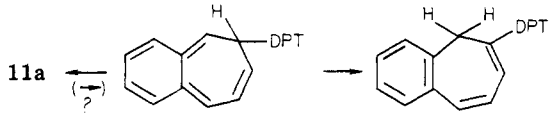
13a



13b

for the endo, such as **13b** and **14**, in which the alkyl substituents are farther apart. However, although repulsion between the 7-DPT and 1- and/or 6-alkyl groups is thus relieved, repulsion between the 7-DPT group and the 3,4 π-bond of the ring would be substantially larger than that between even a *tert*-butyl group and the 3,4 edge. In addition, alkyl substituents attached to the 3,4 edge increase steric interactions between themselves and the endo 7-substituent. Reversion to the NCD structure, in which the C-1–C-6 skeleton becomes planar, offers a way to lower this repulsion.[17] Very low equilibrium concentrations of CHT's **13a** and **14** would not be observable by NMR.

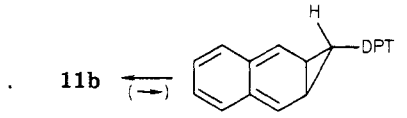
The formation of cycloadduct **11a** without isomerization



15 **16**

to a CHT is an expected consequence of added stabilization imparted to the NCD system by incorporation of one of the double bonds in a benzene ring. Transformation to the CHT tautomer **15** would involve dearomatization of the benzene ring. Consequently, isomerization would require elevated temperatures, and on rearomatization, **15** would be expected to convert to **16** by a hydrogen shift.

Likewise, if one of the double bonds of the CHT is incorporated in a benzene ring, it is stabilized, and **11b** would



17

not equilibrate with **17**, which has a quinoid ring,[18] and compounds of type **17** would be expected to isomerize spontaneously to the 3*H*-benzocycloheptene,[6b] **11b**. The conditions of the experiment, which involved steam distillation, were sufficient to isomerize **17** to **11b**, but even

(10) (a) Hoffmann, R. *Tetrahedron Lett.* **1970**, 2907. (b) Günther, H. *Ibid.* **1970**, 5173. (c) Takahashi, K.; Takase, K.; Toda, H. *Chem. Lett.* **1981**, 689. (d) Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981; pp 197 ff.

(11) (a) Vogel, E.; Wiedemann, W.; Kiefer, H.; Harrison, W. F. *Tetrahedron Lett.* **1963**, 673. (b) Raddick, P.; Rosen, W. *J. Am. Chem. Soc.* **1966**, *88*, 3461. (c) Darius, R.; Thieffull, T.; Pesaro, M.; Eschenmoser, A. *Helv. Chim. Acta* **1963**, *46*, 2893.

(12) (a) Müller, E.; Kessler, H.; Suhr, H. *Tetrahedron Lett.* **1965**, 423. (b) Nozaki, H.; Yamabe, M.; Noyori, R. *Tetrahedron* **1965**, *21*, 1637.

(13) Ciganek, E. *J. Am. Chem. Soc.* **1965**, *87*, 652, 1149.

(14) (a) Betz, W.; Daub, J. *Chem. Ber.* **1974**, *107*, 295. (b) Klärner, F.-G.; Yaslak, S.; Wette, M. *Ibid.* **1979**, *112*, 1168. (c) Balci, M.; Fischer, H.; Günther, H. *Angew. Chem.* **1980**, *92*, 316.

(15) Takeuchi, K.; Arima, M.; Okamoto, K. *Tetrahedron Lett.* **1981**, *22*, 3081.

(16) Heyd, W. E.; Cupas, C. A. *J. Am. Chem. Soc.* **1969**, *91*, 1559; **1971**, *93*, 6086.

(17) We cannot conclusively rule out the presence of a chair conformation, in which the nonbonded repulsion would be relieved with the cost of a probably prohibitive increase in ring strain. However, cycloheptatriene in the vapor phase has been shown to have the boat conformation [Traetteberg, M. *J. Am. Chem. Soc.* **1964**, *86*, 4265], and the NMR spectra of the cycloadducts obtained from decomposition of **1** in various arene substrates could not satisfactorily be accounted for with the absence of a norcaradiene component.

(18) Wittig, G.; Eggers, H.; Duffer, P. *Justus Liebigs Ann. Chem.* **1958**, *619*, 10.

(19) (a) Tsuruta, H.; Mori, S.; Mukai, T. *Chem. Lett.* **1974**, 1127. (b) Hall, G. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 2203. (c) Günther, H.; Tunggal, B. D.; Regitz, M.; Scherer, H.; Keller, T. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 563. (d) Wehner, R.; Günther, H. *J. Am. Chem. Soc.* **1975**, *97*, 923.

Table IV. Equilibria for the Interconversion of Norcaradiene/Cycloheptatriene Tautomers

	aromatic substrate	product	$\delta_{H\text{-}1,6}$[b]	K, 25 °C	NCD, 25 °C, %	T_C, °C
A	benzene	CHT	5.32	<<0.1	~0	
B	toluene	1-Me-CHT	5.15	<<0.1	~0	
C	*o*-xylene	3,4-Me_2-CHT	4.61	0.22	17.9	−100
D	*m*-xylene	2,4-Me_2-CHT	4.50	0.28	21.8	−100
E	*p*-xylene	1,4-Me_2-CHT	4.90	0.08	7.5	−100
F	*p*-ethyltoluene	1-Me-4-Et-CHT	4.75	0.15	12.9	−100[c]
G	*p*-ethyltoluene	7-Et-4-Me-NCD	3.91	0.75	42.9	−60[d]
H	*p*-cymene	1-Me-4-*i*-Pr-CHT	4.63	0.21	17.1	−100[c]
I	*p*-cymene	1-*i*-Pr-4-Me-NCD	3.54	1.3	56.0	−60[d]
J	4-*tert*-butyltoluene	2-Me-5-*t*-Bu-CHT	5.10			
K	4-*tert*-butyltoluene	1-*t*-Bu-4-Me-NCD	3.74	0.97	48.9	−45
L	*p*-diisopropylbenzene	1,4-(*i*-Pr)$_2$NCD	3.34	1.72	63.2	−100
M	mesitylene	1,3,5-Me_3-NCD	3.71	1.00	20.0	−75
N	durene	1,3,4,6-Me_4-NCD (**10a**)				*e*
O	durene	1,2,4,5-Me_4-NCD (**10b**)	2.49	14.6	93.6	−100
P	naphthalene	CHT	4.85			
Q	naphthalene	NCD	>3.26/1.75	>100	100	
R	thiophene	NCD	>2.70/2.34	>100	100	

[a] No stereochemistry is implied.[3] CHT = cycloheptatriene; NCD = norcaradiene. [b] Time averaged value of $\delta_{H\text{-}1,6}$ observed at ambient temperature. [c] Coalescence temperature not clearly observable, but owing to the similarity between F, H, C, D, and E, a value of −100 °C is estimated. [d] Coalescence temperature for G and I not observed directly but is estimated as −60 °C by averaging the values of K and M. [e] No line broadening or other indication of approach to a coalescence temperature down to −90 °C.

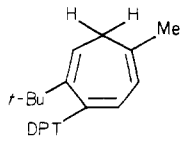
prolonged heating of **11a** above its melting point failed to isomerize it.

At low temperatures, the NCD and CHT isomers in most cases became separately observable by ^{1}H NMR, and a coalescence temperature could be estimated. Although we were not able to achieve satisfactory results in all cases, owing to sharply reduced solubility, difficult resolution, or a very one-sided equilibrium position, values for the H-6 signals of most of them are reported in Table IV. Similar coalescence temperatures were observable for the C-6 signals by ^{13}C NMR.

Only in the case of **5b** (from *p-tert*-butyltoluene) were we able to measure the equilibrium below the coalescence temperature; a ratio of CHT to NCD of 1.3 ± 0.1 could be estimated at ca. −80 °C, corresponding to $\Delta G°$ = 70–130 cal/mol. Alternatively, the equilibrium constants were estimated from the NMR signals of the vinyl hydrogens at C-1 and C-6 of the CHT and the corresponding cyclopropyl hydrogens of the NCD. In these rapidly equilibrating tropilidene systems, a single resonance is seen near room temperature, at a shift position determined by the ratio of the two participating species (see Table IV).

Equilibrium constants can be calculated from them and the value of $\delta_{H\text{-}1,6}$ in the individual isomers. Normally, $\delta_{H\text{-}1,6}$ (CHT) − $\delta_{H\text{-}1,6}$ (NCD) is 2.2 to 3.0 ppm.[18] Although we could not obtain such values with useful accuracy from our NMR spectra, the required chemical shifts could be satisfactorily estimated from the spectra of closely related compounds. A value for $\delta_{H\text{-}1,6}$ (NCD) of 2.31 was obtained from averaging the values of $\delta_{H\text{-}1,6}$ (NCD) from entries O, Q, and R (Table IV), since they exist as NCD's at least to −100 °C. Similarly, entries A, B, J, and P exist wholly as CHT's down to −100 °C with an average value for $\delta_{H\text{-}1,6}$ (CHT) of 5.11 ppm. A difference of 2.8 ppm between $\delta_{H\text{-}1,6}$ (CHT) and $\delta_{H\text{-}1,6}$ (NCD) is in agreement with other observed systems. The values of K shown in Table IV were estimated[20] by using these values in the relation $(5.11 - \delta_{obsd})/(\delta_{obsd} - 2.31) = K$.

Sigmatropic Rearrangements. As reported[2] for the dimethyl- and trimethyltropilidenes, diphenyltriazolyltropilidenes may rearrange to positionally isomeric CHT's upon mild heating. Boiling its solution in benzene was sufficient to bring about quantitative rearrangement of **5b** to **18**. The ^{1}H NMR spectrum of **18**, on which its structural assignment is based, was unusually complex, owing to the presence of conformers and rotamers separated by substantial energy barriers. In addition to the 10-H multiplets diagnostic of the DPT group, the spectrum displayed a 3-H group of multiplets centered at δ 6.04, 5.85, and 5.43 (olefinic H's). The ring-methyl group appeared as three singlets at δ 1.71, 1.58, and 1.51, as did the *tert*-butyl group at 1.12, 1.05, and 0.95. The methylene group appeared as a broad multiplet at δ 1.6. The deduced structure, **18**, is the result of a 1,5-hydrogen shift.



18

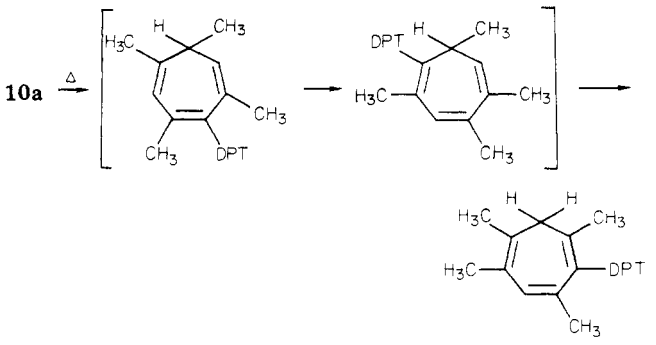
The complexity of the spectrum can be understood in terms of hindered rotation of the DPT and *tert*-butyl groups and the presence of two nonplanar conformations of the CHT ring, as is also observed with the analogous compounds derived from mesitylene and *p*-xylene.[2] Interconversion of the CHT conformations is effectively prevented by steric interactions between the DPT and *tert*-butyl groups, and **18** exists as a nonequilibrium mixture of rotamers and conformers (Scheme I) with an activation energy greater than 20 kcal/mol for inversion of ring conformations.

The possibility exists that two 1,5-hydrogen shifts generated a mixture of structural isomers, but no evidence for such a situation can be found in the rearrangements of analogous compounds.[2]

The rate of rearrangement of **5b** to **18** was followed spectrometrically by measuring the areas of the *tert*-butyl NMR signal in **5b** vs. an internal standard of acetonitrile. The reaction was first order in **5b**; E_a = 24.9±0.4 kcal/mol and $\Delta S^{\ddagger}$ = 14.5 eu.

The thermal rearrangement of NCD **10a** required a considerably higher temperature, 130 °C, than its previously investigated analogues.[2] NMR spectra taken at

(20) Cf. Takeuchi, K.; Fujimoto, H.; Okamoto, K. *Tetrahedron Lett.* **1981**, *22*, 4981, for a similar investigation on 7-aryl-2,5-di-*tert*-butylcycloheptatrienes.

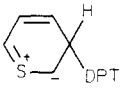


19

periodic intervals indicated that isomerization proceeded through a series of intermediates, for features temporarily appeared that were not present in reactant or product. After prolonged heating, the NMR spectrum corresponded to only a single isomeric CHT. Of the four possible isomers formed by consecutive 1,5-hydrogen shifts, only **19** was consistent with the NMR spectrum. The vinylic proton appeared as a singlet at δ 6.15, the methylene group as a singlet at δ 2.30, and the four methyl groups as singlets at δ 1.90, 1.75, 1.65 and 1.61.

A secondary feature of the rearrangement of **10a** is the final formation of **19**. Previously,[2] only one 1,5-hydrogen shift was observed before a stable CHT was formed. During the isomerization of **10a**, at least two intermediate CHT isomers were formed, the spectra of which could not be obtained singly. However, upon arrival of the migrating hydrogen atom at the 2- or 5-position, rearrangement ceased, indicating that **19** is an energy well for the system. Unfortunately, the complexity of the spectra precluded our obtaining kinetic data on this interesting rearrangement.

Like **11a**, the thiophene analogue, **12**, resisted rearrangement; its ^{1}H NMR spectrum remained unchanged after prolonged heating. Stability of **11a** and **12** to rearrangement does not indicate that they are necessarily in an energy sink but is presumably due to the high energy of the intermediate that would be required in the first step, valence tautomerization by opening of the cyclopropane ring between the bridgehead positions. In the case of **12**, this step would generate a sulfonium ylide, **20**; in the case of **11a**, this step would destroy a benzenoid system and replace it by a quinodimethane system, **15**.



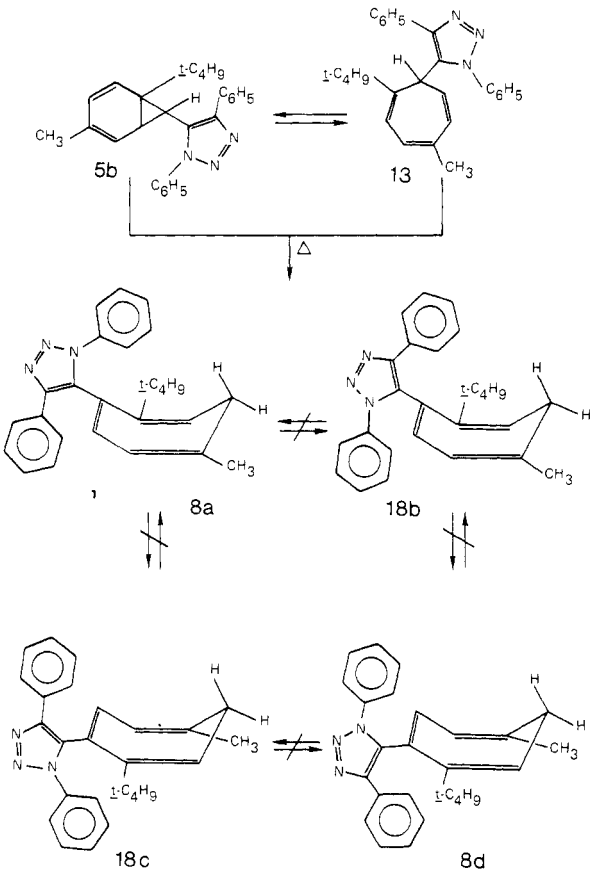
20

Conclusions

The results previously obtained in the xylene series showed how the site selectivity of the carbene was influenced by the position of the alkyl groups.[2] Increasing size of alkyl substituents results in still greater selectivity. In all substrates except *p-tert*-butyltoluene, products from attack of the carbene only at the 1,2 or 3,4 C–C bond of the benzene ring were formed. In the exception, in which attack occurred to a small extent at the 2,3-position, the 1,2-site was still greatly preferred. The site preference changed greatly in going from *p*-ethyltoluene to *p-tert*-butyltoluene; increased size of the alkyl substituent surprisingly favors attack next to the larger substituent, although results with *o*- and *m*-xylene[2] implied that attack occurred more readily at the least crowded positions.

The products from thiophene and naphthalene result from anti orientation of the DPT group with respect to the benzene ring and imply the same preference in the reactions of the other substrates.

Scheme I



The change in the NCD/CHT ratio from **2** (mostly CHT) to **5b**, **10a**, and **10b** (NCD) effected by increasing the number (Table IV, entries E, L, N, O) or bulk (entries G, I, K, L) of alkyl substituents reflects a sterically increased energy content of the CHT tautomer of the tropilidenes. This is inferred to be a direct result of increased steric interaction between the large DPT group and the alkyl substituents. The decreased activation energies for 1,5-hydrogen shifts of examples K and M (Table IV) relative to D and E also support an overall increase in the ground-state free energies of the CHT tautomers. Although factors previously mentioned[11-14] may be the most decisive controls on the NCD/CHT equilibrium, the present results confirm that steric factors may also play a major role, as implied by the observations of Takeuchi, Arima, and Okamoto[15] on *tert*-butylated systems.

Sigmatropic migration of H is resisted by those factors that stabilize the NCD structure, which must first change to the CHT structure.

Experimental Section

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 ^{1}H NMR spectra, which were determined on $CDCl_3$ solutions. A JEOL 100-MHz nuclear magnetic resonance spectrometer with Fourier-transform was used for ^{13}C NMR and variable-temperature spectra. Column chromatography was done on Woelm neutral alumina or silica gel with fluorescent indicator. Elemental analyses were by Spang Microanalytical Laboratory, Eagle Harbor, MI.

Solutions of 5-(diazomethyl)-1,4-diphenyl-1,2,3-triazole (**1**)[5] ranging in concentration from 0.01 to 0.02 M were prepared in carefully dried equipment by dissolving the diazo compound in the appropriate amount of aromatic substrate. In the cases in

which the aromatic substrate was a solid, methylene chloride was used as a solvent. The resulting bright red solutions were then flushed with a stream of dry nitrogen gas for a minimum of 1 h, agitated by magnetic stirring, and then immersed in an oil bath preheated to 45 to 55 °C. A positive pressure of nitrogen was maintained throughout the decomposition, which was complete after 4 to 5 h, at which time the mixture was allowed to cool to room temperature. The workup procedures are described for the individual substrates.

Decomposition in *p*-Ethyltoluene. Thermolysis of 400 mg (1.5 mmol) of 1 in 25 mL of *p*-ethyltoluene gave a yellowish solution, which was filtered to remove a small amount of 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde azine.[5] The excess *p*-ethyltoluene was removed by vacuum distillation (0.1 mm) at room temperature, leaving a viscous, yellow oil, which was triturated with three 25-mL portions of petroleum ether (bp 30–60 °C). The combined extracts were refrigerated, whereupon 365 mg (68%) of a white, crystalline material precipitated, mp 121–126 °C. The ^{1}H NMR spectrum indicated two isomeric adducts in ca. 1:1 ratio; however, all attempts to separate them failed. On the basis of the relative intensities, and with the aid of decoupled spectra, the two adducts were identified as 1-methyl-4-ethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (**3a**) and 1-ethyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (**3b**) (see Table I for NMR). An analytical sample of the mixture was prepared by two recrystallizations from absolute ethanol: mp 129–130 °C; mass spectrum, *m/e* 353. Anal. ($C_{24}H_{23}N_3$) C, H, N.

Decomposition in *p*-Cymene. Thermolysis of 520 mg (2 mmol) of 1 in 75 mL of freshly distilled *p*-cymene gave a yellowish solution. The excess *p*-cymene was removed by vacuum distillation (0.1 mm) at 40 °C. The residue, 600 mg (87%), was purified on 2-mm preparative silica TLC plates by elution with benzene/ethyl acetate (20:1). The two major bands were removed by extraction with ethyl acetate. The first fraction, 275 mg (39%) of a clear oil, crystallized from a diethyl ether/petroleum ether (30–60 °C), mp 159–162 °C. The adduct was identified by ^{1}H NMR as 1-methyl-4-isopropyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (**4a**). Recrystallization from diethyl ether/petroleum ether (bp 30–60 °C) (1:1) afforded an analytically pure sample: mp 162.5–163.5 °C; see Table I for NMR; mass spectrum, *m/e* 367. Anal. ($C_{25}H_{25}N_3$) C, H, N.

The second fraction, 325 mg (48%), a clear oil, was identified by ^{1}H NMR (Table I) as 1-isopropyl-4-methyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (**4b**): mass spectrum, *m/e* 367. All attempts to crystallize **4b** failed. Column chromatography (25 g of Florisil, elution with benzene) afforded an analytically pure oil. Anal. ($C_{25}H_{25}N_3$) C, H, N.

Decomposition in *p*-*tert*-Butyltoluene. Thermolysis of 400 mg (1.5 mmol) of 1 in 50 mL of reagent-grade 4-*tert*-butyltoluene gave a yellowish solution. The brownish-yellow residue remaining after vacuum distillation (0.1 mm) at 45 °C was titurated with petroleum ether (bp 30–60 °C), yielding 435 mg (75%) of a white, crystalline material, mp 151–153 °C. The ^{1}H and ^{13}C NMR spectra indicated the presence of two isomeric adducts in ca. 1:7 ratio; however, neither repeated recrystallizations nor chromatography brought about separation. On the basis of the relative intensities and with the aid of decoupled spectra, the major isomer was identified as 4-methyl-1-*tert*-butyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (**5b**); the minor isomer was deduced to be 5-methyl-2-*tert*-butyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl]cycloheptatriene (**6**) (see Tables I and II for NMR). Two recrystallizations from absolute ethanol gave an analytically pure mixed sample: mp 154–155.5 °C; mass spectrum, *m/e* 381. Anal. ($C_{26}H_{27}N_3$) C, H, N.

Decomposition in *p*-Diisopropylbenzene. Thermolysis of 522 mg (2 mmol) of 1 in 70 mL of reagentgrade *p*-diisopropylbenzene gave a yellow solution, which was filtered to remove small amounts of aldazine. The viscous, yellow oil remaining after vacuum distillation (0.1 mm) at 50 °C was chromatographed on a column of 50 g of Florisil (60–100 mesh), which was eluted with benzene/diethyl ether (10:1). The clear oil thus obtained was dissolved in a diethyl ether/petroleum ether (bp 30–60 °C) mixture and cooled, whereupon 632 mg (80%) of a white crystalline material precipitated, mp 145–150 °C. The ^{1}H NMR spectrum indicated the presence of two 1:1 adducts. All attempts to separate them by crystallization or chromatography failed. On the basis of the relative intensities in the NMR spectrum (Table I) and with the aid of decoupled spectra, they were identified as 1,4-diisopropyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (**7**) and 5-[2-(4-isopropylphenyl)prop-2-yl]-1,4-diphenyl-1,2,3-triazole (**8**). Recrystallization twice from ethanol gave an analytically pure mixture of isomers: mp 151–153 °C; mass spectrum, *m/e* 395. Anal. ($C_{27}H_{29}N_3$) C, H, N.

Decomposition in *p*-Di-*tert*-butylbenzene. Thermolysis of 522 mg (2 mmol) of 1 in 25 g of recrystallized *p*-di-*tert*-butylbenzene dissolved in 50 mL of dichloromethane gave a reddish-brown solution, which was freed from excess substrate 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. TLC examination revealed the presence of at least seven components. Separation by preparative TLC on silica gel furnished only the component of highest R_f in reasonably pure form. Recrystallization of this fraction from acetone afforded 55 mg (16%) of a white solid, mp 171–173 °C, identified as 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde (NMR, IR, and mixture melting point). All fractions were examined by ^{1}H NMR spectroscopy; however, none displayed olefinic absorptions. It was concluded that no products derived from cycloaddition of the carbene to the substrate nucleus were formed during the thermolysis.

Thermal Rearrangement of 5b. A solution of 250 mg (0.6 mmol) of **5b** in 20 mL of reagent-grade benzene was refluxed for 24 h. The benzene was removed under aspirator vacuum, leaving 250 mg of a yellow oil, which was chromatographed on 25 g of Florisil (60–100 mesh). The column was eluted with a benzene/diethyl ether mixture (10:1), and each fraction was examined by TLC after concentration. Only one fraction was isolated, 225 mg (90%) of a colorless oil, 1-methyl-5-*tert*-butyl-4-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (**18**). The oil was dissolved in a minimum amount of diethyl ether; an equal portion of petroleum ether (bp 30–60 °C) was added, and the resulting solution was cooled, whereupon a white crystalline material precipitated: mp 146–147.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.70 (m, 2 H), 7.40 (m, 8 H), 6.04, 5.85, and 5.43 (m, 3 H), 2.60 (br m, 2 H), 1.71, 1.58, and 1.51 (s, 3 H), 1.12, 1.05, and 0.95 (s, 9 H); mass spectrum, *m/e* 381. Anal. ($C_{26}H_{27}N_3$) C, H, N.

Kinetics for the Thermal Isomerization of 5b. The rates of isomerization of **5b** were determined in sealed NMR tubes containing 20 to 50 mg of adduct in $CDCl_3$ and placed in a constant-temperature vapor. The kinetic data were obtained by measuring the areas of the *tert*-butyl signal of **5b** relative to an internal standard of acetonitrile. Prior to isomerization, all tubes were examined by ^{1}H NMR spectroscopy for purity and adequate concentration. The first-order rate constants, determined graphically, were as follows: 101.0 °C, 4.24×10^{-5} (deviation 5.6%); 107.0 °C, 7.88×10^{-5} (deviation of 12.1%); 117.0 °C, 17.2×10^{-5} (deviation 5.5%); 130.5 °C, 50.3×10^{-5} s^{-1} (deviation 5.6%); for the mean temperature 110 °C, E_a = 25 kcal/mol; $\Delta H^{\ddagger}$ = 24 kcal/mol; $\Delta S^{\ddagger}$ = −15 eu; log A = 10.2 s^{-1}.

Decomposition in Durene. Durene was removed by steam distillation from the mixture resulting from reaction of 50 g of durene and 0.522 g (0.002 mol) of 1 in 100 mL of dichloromethane. The residue was exhaustively extracted with chloroform, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered, and the filtrate was concentrated under aspirator vacuum to leave 720 mg of white crystalline material, mp 133–179 °C. Sublimation of the residue removed the remaining durene impurity. The residue was then triturated with three 30-mL portions of petroleum ether (bp 30–60 °C), which were combined and then cooled in an ice bath. A white solid (320 mg, 45%) formed and was isolated by filtration, mp 187–193 °C. On the basis of the NMR spectrum (Tables I and II), it was identified as **1,3,4,6-tetramethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (10a)**. Four recrystallizations from absolute ethanol gave an analytically pure sample: mp 201–202.5 °C; mass spectrum, *m/e* 367. Anal. ($C_{25}H_{25}N_3$) C, H, N.

The mother liquor was concentrated, giving an additional 82 mg (11%) of a clear oil. Its NMR spectrum consisted of that for ca. 25% of **10a** plus that of another compound (**10b**, Table I). The second spectrum agrees with the structure of 1,2,4,5-tetramethyl-7-(1,4-diphenyl-1,2,3-triazol-5-yl)norcaradiene (**10b**), the

isomeric adduct from the carbene addition to durene.

Decomposition in Naphthalene. In the manner of the foregoing experiment, 50 g of recrystallized naphthalene and 0.522 g of 1 gave rise to 1.26 g of white crystalline material, which showed three components by TLC.

The crude mixture was dissolved in a minimal mount of benzene and chromatographed on a column packed with 50 g of alumina (100–200 mesh). The column was eluted with benzene, and each fraction was examined by TLC after concentration, and ones of similar composition were combined. The first fractions amounted to 600 mg of naphthalene; the second fraction, 420 mg (58%), mp 195–198 °C, was identified by NMR (Table I) as **7-(1,4-diphenyl-1,2,3-triazol-5-yl)-2,3-benzonorcaradiene (11a)**. Two crystallizations from absolute ethanol gave an analytically pure sample: mp 203–204.5 °C; mass spectrum, *m/e* 361. Anal. ($C_{25}H_{19}N_3$) C, H, N.

The third fraction (240 mg, 41;), mp 192–196 °C, was assigned the structure **7-(1,4-diphenyl-1,2,3-triazol-5-yl)-3,4-benzocycloheptatriene (11b)**, based on the NMR spectrum (Table I). A portion of this material was purified on a 2-mm preparative silica TLC plate by elution with a benzene/ethyl acetate (20:1) mixture; **11b** was removed from the silica gel by extracting with ethyl acetate, and the extract was concentrated under aspirator vacuum, whereupon **11b** crystallized, mp 196–201 °C. Two recrystallizations from absolute ethanol gave an analytically pure sample: mp 201–202 °C; mass spectrum, *m/e* 361. Anal. ($C_{25}H_{19}N_3$) C, H, N.

A sample of **11a** was fused and kept at 210 °C for 15 min; on cooling, it was unchanged except for a tint of yellow. Heating at 210 °C for an additional 10 min brought about no change, but further heating caused darkening and evident decomposition.

Decomposition in Thiophene. Thermolysis of 0.522 g (0.002 mol) of 1 in 70 mL of freshly distilled thiophene gave a yellow solution, which was filtered to remove a small amount of 1,4-diphenyl-1,2,3-triazole-5-carboxaldehyde azine.[15] The excess thiophene was removed by vacuum distillation (0.1 mm) at room temperature, leaving a viscous yellow oil, which was triturated with three 25-mL portions of petroleum ether (bp 30–60 °C). The combined extracts were refrigerated, whereupon 405 mg (60%) of a white, crystalline solid, mp 177–185 °C, precipitated. On the basis of the NMR spectrum (Table I), the adduct was identified as **6-(1,4-diphenyl-1,2,3-triazol-5-yl)-2-thiabicyclo[3.1.0]hex-3-ene (12)**. The spectrum was unchanged when a solution of **12** in $CDCl_3$ was heated at 107 °C for 12 h in a sealed tube. Two recrystallizations from an ethanol/petroleum ether (bp 30–60 °C) mixture yielded analytically pure material, mp 191–192 °C. Anal. ($C_{19}H_{15}N_3S$) C, H, N, S.

Thermal Rearrangement of Norcaradiene (10a). A sealed tube containing 50 mg of analytically pure **10a** in $CDCl_3$ (1% Me_4Si) was placed in a vapor bath of refluxing isoamyl alcohol (bp 130 °C). At periodic intervals the tube was removed, cooled to room temperature, and examined spectroscopically (NMR). After heating at this temperature for 24 h, no subsequent changes were observed. On the basis of the ^1H NMR spectrum, the original solute had been isomerized entirely to 1,3,5,6-tetramethyl-2-(1,4-diphenyl-1,2,3-triazol-5-yl)cycloheptatriene (**19**): NMR ($CDCl_3$) δ 7.72 (m, 2 H), 7.30 (m, 8 H), 6.15 (s, 1 H), 2.30 (s, 2 H), 1.90 (s, 3 H), 1.75 (s, 3 H), 1.65 (s, 3 H), 1.61 (s, 3 H).

Registry No. **1**, 15764-89-3; **2**, 75918-84-2; **3a**, 87185-25-9; **3b**, 87185-27-1; **4a**, 87185-26-0; **4b**, 87185-28-2; **5a**, 87185-30-6; **5b**, 87185-29-3; **6**, 87185-31-7; **7**, 87185-32-8; **8**, 87185-33-9; **10a**, 87185-34-0; **10b**, 87185-35-1; **11a**, 87185-36-2; **11b**, 87185-37-3; **12**, 87185-38-4; **18**, 87185-39-5; **19**, 87189-84-2; 1,3,5-MeNCD, 87185-40-8; CHT, 544-25-2; 1-MeCHT, 3045-88-3; 3,4-CHT, 78968-78-2; 2,4-CHT, 71457-57-3; 1,4-CHT, 66729-58-6; *p*-cymene, 99-87-6; *p*-*tert*-betyltoluene, 98-51-1; *p*-diisopropylbenzene, 100-18-5; durene, 95-93-2; naphthalene, 91-20-3; thiophene, 110-02-1; *p*-di-*tert*-butylbenzene, 1012-72-2; (1,4-diphenyl-1*H*-1,2,3-triazol-5-yl)methylene, 63296-69-5; benzene, 71-43-2; toluene, 108-88-3; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; mesitylene, 108-67-8; *p*-ethyltoluene, 622-96-8.

Involvement of Neighboring Chlorine in the Exchange Reactions of Iodine Monochloride and Vicinal Organic Iodochlorides

George H. Schmid* and James W. Gordon

Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada

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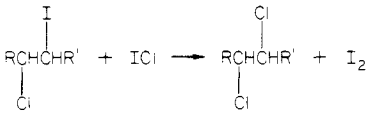
The reaction of vicinal organic iodochlorides and ICl in CCl_4 at 25 °C forms vicinal organic dichlorides and iodine. The rate law for this exchange reaction of ICl and 2-chloro-3-iodo-2,3-dimethylbutane is overall third order: second order in ICl and first order in iodochloride with a value of $k_3 = 7.2 \pm 0.9$ M^{-2} s^{-1}. Stereospecific exchange occurs in the reaction of ICl and *erythro*- and *threo*-2-chloro-3-iodobutane. Thus the erythro isomer forms only *meso*-2,3-dichlorobutane while the threo isomers form only the *dl* dichloride. Nonstereospecific exchange occurs in the reaction of ICl and *erythro*- and *threo*-1-chloro-2-iodo-1-phenylpropane. The data support a mechanism involving a cationic intermediate. In addition, the chlorine atom is involved in the reaction prior to the product-determining step.

Iodine monochloride (ICl) has been known for years to react with organic iodides to form an organic chloride and iodine.[1] We have found that a similar exchange reaction occurs between ICl and vicinal organic iodochlorides to form iodine and vicinal organic dichlorides according to the eq 1. In this paper, we present evidence that these



(1)

two exchange reactions are similar in that they have the same stoichiometry and follow the same rate law. However, in the reaction of vicinal organic iodochlorides, the chlorine atom is involved in the reaction prior to the product-determining step.

Table I. Rate Data for the Exchange Reaction of ICl and 2-Chloro-3-iodo-2,3-dimethylbutane in CCl_4 at 25 °C

(*vic*-iodochloride)$_0$, M	$(ICl)_0$, M	k_{app}, M^{-1} s^{-1}	k_3, M^{-2} s^{-1}
0.034 89	0.004 41	0.249 ± 0.003	7.14
0.034 89	0.001 60	0.201 ± 0.003	5.75
0.017 00	0.002 59	0.139 ± 0.001	8.17
0.017 44	0.001 60	0.123 ± 0.001	7.05
0.006 98	0.001 60	0.0549 ± 0.0004	7.87

[a] Average 7.2 ± 0.9.

(1) (a) Geuther, A. *Justus Liebigs Ann. Chem.* **1862**, *123*, 124. (b) Friedel, C. *Ibid.* **1865**, *135*, 206.

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