THE EFFECTS OF MULTIPLICITY AND EXCITATION ON THE BEHAVIOR OF 2-METHYL-2-PHENYLPROPYLIDENE; THE INTRAMOLECULAR CHEMISTRY OF 2,2-DIPHENYLPROPYLIDENE

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The intramolecular reactions of 2-methyl-2-phenylpropylidene and 2,2-diphenylpro-Abstract. pylidene have been determined.

The behavior of the neophyl carbene (2-methyl-2-phenylpropylidene, 2) has been important to the theory of divalent carbon.¹ Thus 1-diazo-2-methyl-2-phenylpropane (1, Eq 1) has been reported (Table 1) to decompose at 59°C via 2 to 1-methyl-1-phenylcyclopropane (3) by carbonhydrogen insertion, 2-methyl-1-phenylpropene (4) by phenyl migration, (Z, 5) and (E, 6)-2phenyl-2-butenes by methyl migration, unidentified terminal olefins and 2-methyl-2-phenylpropanal azine.^{1a} More recently^{1b} thermolysis, photolysis and triplet photosensitization of 1



were found (Table 1) to yield 2-methyl-3-phenylpropene (7) and 2-phenyl-1-butene (8) in significant quantities along with 3-6 and 2-methyl-2-phenylpropanal azine. To explain the varying yields of 3-6 and in particular formation of 7 and 8 by two fold rearrangements of 2, the hydrocarbon products were presumed to be formed by competitive singlet and triplet processes which vary in extent according to the decomposition method. Of interest thus is that 7 and 8 might arise (Eq 2) from triplet neophyl carbene (9) upon hydrogen abstraction, spin-pairing and then phenyl and methyl migrations. Similar overall processes (Eq 2) may be envisaged for singlet (12) and excited singlet neophyl carbenes involving hydride transfer and rearrangement of dipolar intermediate 11. Further, paths to 7 and 8 could involve various reactions of 1 which by-pass 9 and/or 12.^{1c}



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A study is now reported of (1) thermal decomposition of sodium (13) and lithium (14) salts of 2-methyl-2-phenylpropanal <u>p</u>-tosylhydrazone^{2a} and (2) thermolysis, triplet photosensitization and photolysis of 3-(2-phenyl-2-propyl)diazirine $(15)^{2b}$ and 1, respectively. This investigation reveals that the previous experiments^{1a,b} are seriously complicated by apparent competitive cationic processes and the conclusions reached therefrom are significantly incorrect. The behavior of 1-diazo-2,2-diphenylpropane (16) as generated from sodium (17) and lithium (18) salts of 2,2-diphenylpropanal <u>p</u>-tosylhydrazone has also been determined. Diazopropane 16 is of interest because of its possible double rearrangement decomposition reactions.

In the present study the behavior of 1 was initially evaluated by thermolysis of 13 and 14 in aprotic environments. At 160-200°C in triglyme 13 decomposes (> 60% yield) in the presence of sodium methoxide (0.5-9.0 equiv) to 3, 4 and 6 (Table 1). Carbon-hydrogen insertion yielding 3 and phenyl migration to 4 are the principal carbenic processes. Rearrangement of a methyl group in 2 to give 6 is minor. Of particular significance is that 7 and 8 as possibly derived from two fold rearrangements of 2 (Eq 2) are not obtained. In experiments to determine whether 7 and 8 had been initially formed in the decompositions of 13 and then isomerized completely to 4 and 6. 7 was found at maximum to be only 17% converted to 4 and 8 is inert. Olefins 7 and 8 are thus not formed in thermolysis of 13 at 160-200°C. At 80-120°C however, decomposition of 13 is altered in that conversions to 3 are lowered, rearrangement to 4 is increased and formation of 5, 7 and 8 becomes evident. Thermolysis of 14 at 200°C gives less 3 and more 5-8 than does 13. At 80°C conversion of 14 to 3 is greatly increased and 4-8 become pronounced. The responses of 13 at 80-120°C and of 14 at 80-200°C correspond to that of competitive carbenic and cationic decompositions of p-tosylhydrazonates.³

Thermolysis, triplet photosensitization and photolysis of 15 and 1 were then investigated (Table 1) in environments which minimize cationic processes. The carbenic behavior of 15 is satisfactory in hydrocarbons containing tetramethylguanidine and sodium hydride. Diazopropane 1 is much more difficult, however, to purify and protect since it is an acid which catalyzes its self-destruction. Thermolysis (180°C) and photosensitization (25°C) of 15 and 1 yield 3-6 of essentially identical compositions. Since 15 does not give 7 and 8 and 1 results in 7 in no more than 2.3% proportion, double rearrangements as in Eq 2 are insignificant. The experiments also strongly imply that 2, generated as triplet 9 or singlet 12, rearranges and presumably inserts via 12. The behavior of 2 as singlet 12 thus is similar to that of 2-methylpropylidene⁴ and 2,2-dimethylpropylidene⁴ and reinforces the presumption that the barriers for triplet to singlet conversions of alkyl carbenes are not severe kinetic hurdles. The present experiments also reveal that the phenyl/methyl migration aptitude for rearrangement of 2 at 160-200°C is $-9:1.^{5}$

TABLE 1: DECOMPOSITION OF	1-DIAZO-2-METHYL-2-PHENYLPROPANE	(1), SODI	UM (13)	AND LITHIUM	(14)
2-METHYL-2-PHENYLPROPANAL	p-TOSYLHYDRAZONATES AND 3-(2-PHE)	NYL-2-PROP	PYL) DIAZI	RINE (15).	

Reactant	Method	Solvent	Ti	ne	3	4 ~	5	<u>6</u>	<u>7</u>	<u>8</u>	20
1 ^a	Δ, 59°C	^С 6 ^Н 14			43	49	8.5		unidentified ^b		d ^b
1 ^c	∆, 69°C	C6H6			34.2	42.4	2.3	6.1	12.5	2.5 ^b	
1 ^c	hν, ~27°C	C ₆ H ₆			28.3	25.7	6.3	9.7	25.6	4.4 ^b	
1 ^c	^d PS*, ~27°C	C ₆ H ₆			6.8	66.4	2.4	1.9	19.2	3.3 ^b	
13	∆, 200°C	TG ^e	2	min	63.5	33.1	tr	3.4	0	0	
13	∆, 200°C	тс ^f	5	min	65.7	28.8	0	2.7	0	0	
13	Δ, 160°C	tg ^g	5	min	65.4	30.2	0	4.4	0	0	
13	Δ, 120°C	тс ^ћ	15	min	56.5	36.2	3.1	3.5	tr	0.8	
13	Δ, 80°C	тс ^ћ	5	hr	42.6	44.6	3.4	7.6	tr	1.8	
14	Δ, 200°C	тд ¹	5	min	58.4	32.7	3.5	4.1	1.2	tr	
14	Δ, 80°C	τg ⁱ	5	hr	17.5	46.4	3.9	12.2	15.4	4.6	
15	∆, 180°C	C10H18 (NaH)	j		54.7	31.9	8.0	5.4	0	0	
15	^k PS [*] ,TXO,25°C	$C_6 H_6 (TMG)^1$			62.3	30.0	5.8	1.9	0 ^m	0	
15	hν, 25°C	C6H6(TMG)			33.4	31.2	17.7	13.8	tr ^m	0	4.4
1	Δ, 180°C	C10H18 ⁿ	5	min	61.3	31.0	3.1	2.7	1.9	0	
1	^k PS [*] ,TXO,25°C	C ₆ H ₆ (TMG)			55.9	35.6	5.1	1.5	2.3 ^m	0	
1	hν, 25°C	C ₅ H ₁₂ (TMG)			36.1	32.2	10.9	15.5	2.6 ^m	0.2	2.8

(a) Experiment of Ref. la. (b) 2-Methyl-2-phenylpropanal azine is also formed. (c) Experiment of Ref. lb. (d) Fluorenone. (e) Thermolysis in triglyme (TG) and sodium methoxide (8 equiv). (f) NaH (4 equiv). (g) Excess NaOCH₃ (1 equiv). (h) NaOCH₃ (9 equiv). (i) LiOCH₃ (9 equiv). (j) Decalin. (k) 10-Thioxanthone. (l) Tetramethylguanidine. (m) In the absence of a basic protectant, formation of 3 is lowered and 7 and 8 become quite large. (n) Unprotected.

Photolysis of 15 and 1 in basic environments (Table 1) is different from thermolysis and triplet photosensitization in that carbon-hydrogen insertion to 3 is reduced, methyl migration to 5 and 6 is enhanced, and aromatic substitution yields 1,1-dimethylbenzocyclobutene (19, 4.4-3.7%).⁶ The photolytic responses of 15 and 1 resemble those of 3-t-butyldiazirine, 1-diazo-2,2-dimethylpropane, and 3-isopropyldiazirine in solution.⁴ Irradiation of 15 and 1 appears to involve electronically-excited singlet 20 which reacts intramolecularly more indiscriminately than does 12. It cannot yet be concluded, however, that 3-6 are formed totally from excited 20 in these experiments. The phenyl/methyl migratory aptitude for photolysis of 15 and 1 is 2:1 rather than 5:1.^{1b} Formation of 19, though inefficient, is the first example of synthesis of a benzocyclobutene by such an intramolecular capture process.



Decomposition of 16 as generated from 17 at 90-125°C and 18 at 65-90°C in diglyme results

in insertion of 2,2-diphenylpropylidene (21) into its methyl group to give 1,1-diphenylcyclopropane (22; 16-20%), phenyl migration to yield (Z, 23) and (E, 24)-1,2-diphenylpropenes (40-45% and 27-28%, respectively) and formation of 1,1-diphenyl-1-propene (25, trace; < 1%) by methyl migration. 2,3-Diphenyl-1-propene, (26) the product of two fold rearrangement of 21, was not detected. The enhanced migratory ability of a phenyl group in 21 as compared to 2 reveals the activation of the stationary phenyl group for phenyl migration in 21. Of further note is that 18 containing a trace of methanol decomposes to 26 (19%) along with 22 (12%), 23 (36%), 24 (29%) and 25 (trace). This experiment reveals once again the sensitivity of a diazoalkane to a protic environment to give products of cationic decomposition.



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- (2) (a) Prepared in situ from 2-methyl-2-phenylpropanal p-tosylhydrazone and excess sodium or lithium methoxides under vacuum. (b) Synthesized by chromic acid oxidation of 3-(2-phenyl-2-methyl)diaziridine as obtained from 2-methyl-2-phenylpropanal and chloramine. (c) Experiments with 7 and 8 at 160-200°C in the presence of sodium methoxide at much greater concentrations and for longer periods than for the decompositions of 13 of Table 1 revealed that 8 is unaffected and at least 83% of 7 is recovered.
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- (5) The values of 10-20:1¹ reported previously are in error because of the significant cationic rearrangements which occur competitively with the carbenic processes.
- (6) Assigned by MS, NMR and IR methods.

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