Table I. Partial Decomposition of 1-1-d_4 Mixtures in DEC at 144°

% reaction	t, min	Initial mixture 1 + 1-d_4 (mmol)	Total nitrone remaining (mmol)	Nitrone remaining with isotopic composition 1 + 1-d_4 (mmol)^a	f, fraction of original 1 + 1-d_4 remaining
10	61	0.1823	0.164	0.160	0.878
20	129	0.0908	0.0727	0.0680	0.749
30	204	0.0577	0.0404	0.0344	0.596
50	391	0.0548	0.0274	0.0229	0.418

^{a} These values correspond to $\alpha \times$ mmol of total nitrone remaining.

disappearance of nitrone of original composition 1 + 1-d_4 can be derived from the reaction steps in Scheme I making the steady-state approximation for the caged radical pairs 2 and 2-d_4. The integrated first-order rate law is given in eq

$$k' = k_1(k_c + k_d)/(k_c + k_d + k_{-1}) \tag{1}$$

2. The ratio $[1 + 1\text{-}d_4]_t/[1 + 1\text{-}d_4]_0$ is equal to f in Table

$$\ln \frac{[1 + 1\text{-}d_4]_0}{[1 + 1\text{-}d_4]_t} = k't \tag{2}$$

I. Thus $\log f = -k't/2.303$. Indeed, a plot of $\log f$ vs. t is linear passing through the origin. The slope leads to a value of $k' = 3.64 \times 10^{-5}$ sec^{-1}. The true homolysis rate constant, k_1, can then be obtained from eq 3, which is a rearranged form of eq 1. Using a value of 0.58 for k_{-1}/k_c[8] and

$$k_1 = k'(1 + k_d/k_c + k_{-1}/k_c)/(1 + k_d/k_c) \tag{3}$$

$k_d/k_c = 4.10$ (vide supra), $k_1 = 4.05 \times 10^{-5}$ sec^{-1}. The spectroscopically (uv) determined observed first-order rate constant for 1 in diethylcarbitol at 144° is 2.93 × 10^{-5} sec^{-1}.

References and Notes

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(7) The fraction of the O ether product or the fraction of recovered nitrone not formed by a statistical recombination of iminoxy and benzhydryl radicals. This expression assumes that 1 and 1-d_4 were present in equimolar amounts in the original mixture.

(8) The average of r (assumed equal to k_{-1}/k_c) determined at 10 and 20% decomposition is 0.64. Our estimated standard error of r at 10% reaction is ±23% yielding a value of $r = 0.58 \pm 0.13$. The estimated error of r at 20% reaction is 8% giving a value of $r = 0.70 \pm 0.06$. The error is principally due to uncertainty in α_N at early stages of decomposition. The total amount of O ether formed at 10% reaction was 0.0121 mmol of which 0.077 mmol was scrambled. At 20% reaction the corresponding

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The Case against the Phantom Singlet as a Common Intermediate in Carbenic Decompositions of 1-Diazo-2,2-diphenylpropane and 1-Diazo-1,2-diphenylpropane

Sir:

The mechanisms of carbenic rearrangement are subjects of interest.[1] Recently 1-diazo-2,2-diphenylpropane (1) and 1-diazo-1,2-diphenylpropane (3) have been reported[2] to decompose thermally or photochemically to (Z)- and (E)-1,2-diphenyl-1-propenes (6 and 7) having the same cis/trans ratio of 0.66 ± 0.2. Carbenes 2 and 4 are presumed to rearrange by migration of different groups, phenyl in 2 and hydrogen in 4, to give the same ratio of 6 and 7 via a common intermediate, the phantom singlet 5.[2] Intermediate 5 could arise by orthogonal migration of phenyl in 1a and hydrogen in 3a upon loss of nitrogen; overlap of the p orbitals of 5 during rotation of 90° leads preferentially to the thermodynamically favored isomer 7.[2]

$$\text{(1)}$$
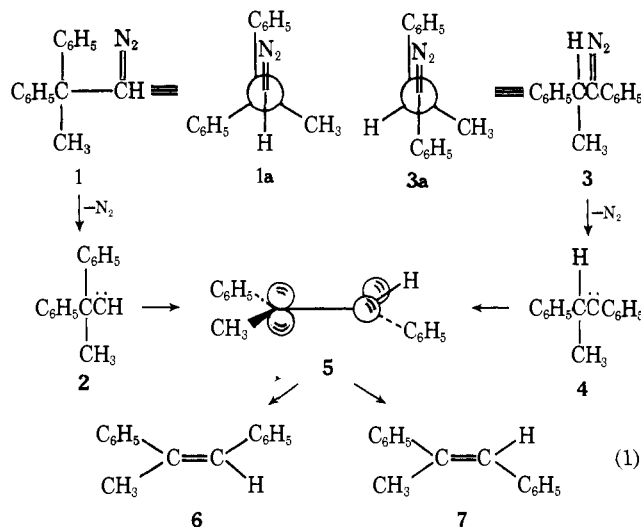
We should now like to summarize our studies of (1) thermolysis of 1 and 3 as generated in situ from 2,2-diphenylpropionaldehyde tosylhydrazone (8)[3] and 1,2-diphenylpropanone tosylhydrazone (9),[3] (2) carbenic and cationic decomposition of pure 1 under various conditions, and (3) aprotic diazotization of 2,2-diphenylpropylamine (10). The present results differ significantly from those reported previously[2] and rule out phantom singlet 5 as a common intermediate in rearrangement of 2 and 4.

It has now been found that the sodium salt of 8 thermolyzes at 160° in diglyme to 6 (45–47%) and 7 (33–35%) along with 1,1-diphenylcyclopropane (11, 19%). The ratios of 6:7 in six such pyrolyses range from 1.29 to 1.42:1.[4] Thus the major product of phenyl migration in decomposition of 1, a presumed intermediate, is 6, the less stable stilbene, rather than 7. Furthermore there is produced 11, the product of in-

sertion into the methyl group of **2**; such a process was not observed in the prior decompositions of **1**.[2]
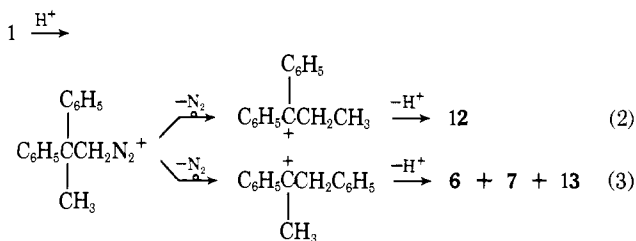

11

12
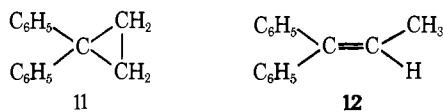
Aprotic decomposition of **9** is decidedly different than **8**. Thus **9** is converted in the presence of sodium hydride (1.1–2.4 equiv) at 160° to **6** (22.5–20.8%) and **7** (60.2–58.9%) along with 1,1-diphenyl-1-propene (**12**, 17.3–20.3%), a product of phenyl migration in **4**. Under the conditions for decomposition of **9**, neither sodium hydride, the sodium salt of **9**, nor sodium p-toluenesulfinate isomerize **6** or **7**. Hydrogen migration in **4** thus gives the more stable olefin **7** rather than **6** as the product of kinetic control. The ratios of **6:7** in these experiments are ~0.375 and quite different from that from **8**. The present results are grossly similar to those reported previously[2] for hydrogen migration in **4**. The rearrangement to **7** is, however, more extensive than previously observed.[2]

An investigation was then made of preparation and decomposition of **1**, the diazopropane presumably generated previously *in situ* from the sodium salt of **8**. Synthesis of **1**, an orange solid of mp *ca.* −5°,[5] has been effected by reaction of dinitrogen tetroxide and ethyl *N*- 2,2-diphenylpropylcarbamate in chloroform at 0° in the presence of sodium acetate and decomposition of the resulting ethyl *N*- nitroso-*N*- 2,2-diphenylpropylcarbamate with sodium methoxide in ether at −20°.

Neat **1** was first decomposed by warming from −20 to 155° in several minutes under nitrogen in alkali-washed baked glass. The products are **6** (33.5%), **7** (45.5%), **11** (12%), **12** (5.5%), and 2,3-diphenyl-1-propene (**13**, 3.5%).

13
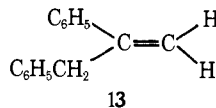
The ratio of **6:7** is 0.74 and thus would appear to agree with that reported by the earlier workers.[2] However, formation of **12** and **13** implies that these olefins, and also **6** and **7** in part, are derived from **1** by carbonium ion processes (eq 2 and 3). Study of **1** was then made under conditions much more favorable to carbenic decomposition.

$$1 \xrightarrow{H^+}$$

$$C_6H_5CCH_2N_2^+ \begin{array}{c} \underset{\overset{-N_2}{\Delta}}{\nearrow} \end{array} \overset{C_6H_5}{\underset{+}{C_6H_5CCH_2CH_3}} \xrightarrow{-H^+} 12 \qquad (2)$$

$$\underset{CH_3}{|} \begin{array}{c} \underset{\overset{-N_2}{\Delta}}{\searrow} \end{array} \overset{+}{\underset{CH_3}{C_6H_5CCH_2C_6H_5}} \xrightarrow{-H^+} 6 + 7 + 13 \qquad (3)$$

To minimize the opportunity for **1** to undergo acid-catalyzed processes, crystalline **1** at −20° was dropped directly under nitrogen into dry, base-treated Pyrex at 160° with instantaneous decomposition. The products of these thermolyses are **6** (43–44.5%), **7** (32.5–33%), **11** (18.5%), **12** (4–3%), and **13** (2–1%). The data reveal a ratio for **6:7** of 1.32–1.35 along with a significant change in the product distribution when compared with the slower decompositions of neat **1**. These experiments emphasize how sensitive the decomposition of **1** is to environment.

Of greater importance is that the ratio of **6** and **7** and the product distribution from rapid decomposition of **1** closely parallel that for base-catalyzed aprotic decomposition of **8**.

Table I. Aprotic Diazotization of **14** and Protic Decomposition of **1** at 160° in Diglyme

Method	Products, %				
	6	7	11	12	13
14 + HNO₂	9	36	0	12.5	42.5
1 + HCl	25.5	56	5	8.5	5
1 + H₂O	25	48	3	6	18

Formation of **11** and **12** could not be completely eliminated, however, upon rapid heating of **1**. A likely or partial source of the **12** and **13** obtained is that **1** is an acid[6a] and effects competitive cationic decomposition of itself (eq 2 and 3). Such self-catalyzed decompositions of primary diazo compounds become much more important at lower temperatures.[6b] It thus appears that the previous researchers have observed partially protic rather than completely carbenic decomposition of **1**.[2] This conclusion is supported by the fact that in the prior work[2] **11**, a product expected from carbenic reaction of **2** and found to be extensive in the present study, was not reported. Further, **12** observed previously[2] as a significant product (17%) is almost eliminated in the present rapid pyrolytic experiments.

To obtain more direct information with respect to the 2,2-diphenyl-1-propyldiazonium ion processes presumed above (eq 2 and 3), aprotic diazotization of 2,2-diphenyl-propylamine (**10**) by isoamyl nitrite and acetic acid in diglyme at 160°[7] and decompositions of **1** in the presence of hydrochloric acid (trace) and of water in diglyme at 160° were investigated. The products (Table I) of diazotization of **14** are consistent with that for the presumed cationic process above, and the ratio of **6:7** of 0.25 is (as now expected) less than that (0.66 ± 0.2)[2] of the study prior to ours. It is relevant that **1** decomposes in the presence of hydrochloric acid or water to give stilbenes **6** and **7** in ratios of 0.46 and 0.52, respectively, along with the insertion product **11** and the propenes **12** and **13** of cationic rearrangement. The **6:7** ratios for these cationic experiments are well within those of the previous report, and support the contention that carbonium ion processes during decomposition of **1** lead to the enhanced formation of **7**.[2]

Along with the conclusion that carbenic decompositions of **1** and **3** do not involve the common intermediate **5**, a result of interest is that migration of phenyl in **2** leads to **6** rather than **7**. Rearrangement of phenyl to give preferentially the less stable stilbene **6** is different than that for alkyl groups in various carbenes in that the latter systems give predominantly the more stable olefins.[8] The stereochemistry of carbenic rearrangement of aryl and related participating groups is a subject of prime concern of this laboratory.

References and Notes

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(3) All new compounds indicated have proper analyses and spectra.

(4) Similar results were also obtained upon decomposition of **8** in the presence of excess butyllithium or sodium methoxide.

(5) Diazopropane **1** is reported to be a yellow liquid.[2] The present **1** on the basis of nitrogen evolution from acetic acid-catalyzed decomposition of a weighed sample, is 100% pure.

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Table I. Product Distribution Obtained from Bicyclo[4.2.1]nona-2,4,7-trien-9-yl Derivatives

| Reaction	Yield (%)	Product distribution (%) 6	7	11	12	13
8, CH₃OH, 0.66 N NaOCH₃ hv,[b] 25°	96	40.9	6.3	46.4	3.4	1.0[a]
syn-**1**, CH₃OH, lutidine (1.4 equiv), 25°, 10 days	98	91.1	1.0		6.8	1.1
syn-**1**, CH₃OH, lutidine (1.4 equiv), 1.5 hr reflux	92	83.7	7.9		8.4	
anti-**1**, CH₃OH, lutidine (1.4 equiv), 1.5 hr reflux	93	84.0	7.2		8.8	

[a] 2% of unidentified material. [b] A 70-W medium-pressure mercury arc, Pyrex vessel.

Table II. Rates of Methanolysis of *syn*-**1** and *anti*-**1**[11]

——*syn*-**1**[a]——		——*anti*-**1**[b]——	
Temp, °C	10⁴k, sec⁻¹	Temp, °C	10⁴k, sec⁻¹
50.80	1.49	51.90	1.85
52.40	1.79	54.40	2.38
54.65	2.40	57.90	3.83
55.90	2.78	60.30	4.57
57.90	3.30		
58.95	3.58		
59.85	4.13		

[a] $\Delta H^* = 22.9 \pm 0.9$ kcal, ΔS^* (55°) $= -5.5 \pm 2.8$ eu. [b] $\Delta H^* = 23.4 \pm 0.9$ kcal, ΔS^* (55°) $= -3.8 \pm 2.9$ eu.

Bicyclo[4.2.1]nona-2,4,7-trien-9-yl Cations Generated by Deamination and Solvolysis

Sir:

The bicyclo[4.2.1]nona-2,4,7-trien-9-yl cation has evoked interest because of its potential homoaromaticity[1] and bicycloaromaticity.[2] The solvolysis of *syn*-bicyclo-[4.2.1]nona-2,4,7-trien-9-yl *p*-toluenesulfonate (**1**) afforded *exo*-dihydroindenyl acetate (**5**)[3] and/or indene,[4,5] depending on the reaction conditions. **1**-9-*d* produced **5** and **7** with effectively all of the deuterium at C-2.[3,5] This result eliminates the possibility of a simple 1,2 shift of carbons 1 or 6 to the C-9 cationic center. Interaction of the monoene and diene units of the cation, visualized by structures **2** and **3** of the intermediate, has been suggested to account for the observed path of rearrangement.

5, X = OAc
6, X = OCH₃
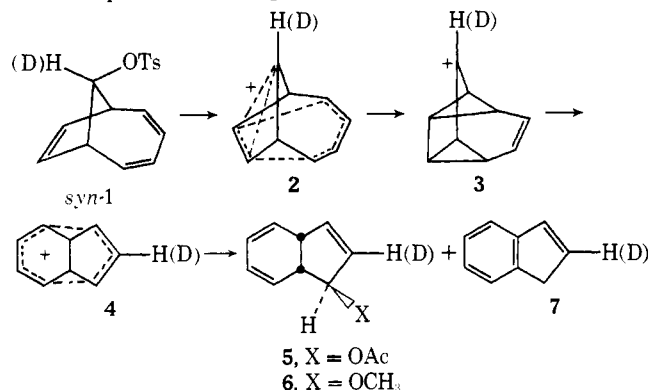
The process leading from **1** to **3** involves an appreciable change of the reactant geometry ("nonvertical" ionization). In reactions of this type the results of tosylate solvolysis and deamination may differ substantially. Solvolysis, with its transition state "late" on the reaction coordinate, favors relocation of atomic nuclei such as to achieve a minimum energy path. Deamination, on the other hand, starting from the highly energetic diazonium ion, passes its transition state "early" and without significant distortion of nuclear positions ("vertical" ionization).[6] Consequently, deamination may produce cations of undistorted geometry which are bypassed in solvolysis (leading directly to more stable bridged species). *We report here that the bicyclo-[4.2.1]nona-2,4,7-trien-9-yl cation generated by deamination can be trapped by nucleophiles and rearranges by simple 1,2 shifts.*

Photolysis of bicyclo[4.2.1]nona-2,4,7-trien-9-one tosylhydrazone (**8**)[4] in CH₃OH-CH₃ONa afforded *syn*-9-methoxybicyclo[4.2.1]nona-2,4,7-triene (**11**) and **6** as the major products. Minor products were *endo*-dihydroindenyl methyl ether (**12**), indenyl methyl ether (**13**), and indene (Table I). Photolysis of tosylhydrazone sodium salts generates diazo compounds[8] which are protonated by protic sol-

vents to give diazonium ions and products derived therefrom.[9] Both syn and anti diazonium ions may be involved in the present reaction. Photolysis of **8** in CH₃OD-CH₃ONa introduced deuterium at C-9. The nmr spectrum of **6**-*d* which was isolated from the CH₃OD photolysis revealed distribution of deuterium over the bridgehead positions; the intensity of each of the bridgehead hydrogens was reduced to half and the large vicinal coupling ($J = 12.5$ Hz) observed with **6** was absent in **6**-*d*. Obviously, the *cis*-dihydroindenyl cation produced from **9** arises by a shift of carbons 2,5 from carbons 1,6 to carbon 9. **11**-*d* was also isolated and shown to carry all of the label at C-9 (no signal of H-9 was observed in the nmr spectrum).

12 **13**
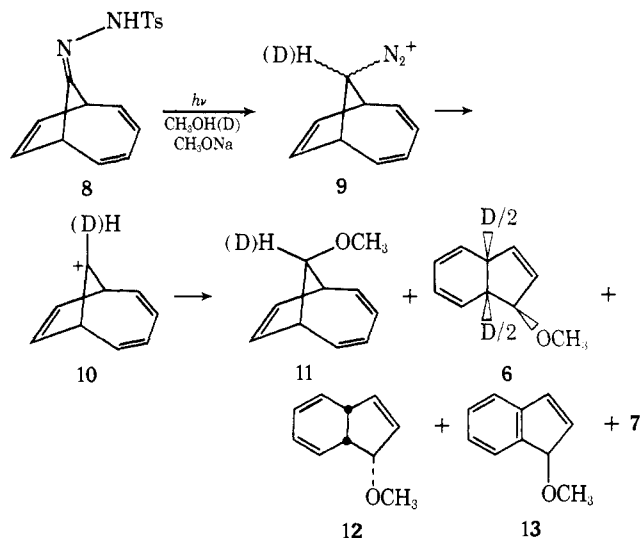
The dramatic differences between the deamination of **9** and the previously studied solvolysis of *syn*-**1** might be due to different reaction conditions rather than to different leaving groups. Therefore, we have solvolyzed **1** in methanol. Our results (Table I) differ from those obtained by Diaz, *et al.*,[3] in acetic acid only by the detection of some *endo*-dihydroindenyl ether (**12**). Significantly, the solvoly-