# Carbene Rearrangements as a Source of the Phantom Singlet State of 1,2-Diphenylpropene

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**Abstract:** Thermal, photochemical, and photosensitized decompositions of 1,2-diphenyldiazopropane (**1**) have been shown to yield (*Z*)- and (*E*)-1,2-diphenylpropenes (**4** and **5**) and 1,1-diphenyl-1-propene (**8**) along with $\alpha$-phenylpropiophenone (**6**), and its azine (**7**) in varying amounts depending on the conditions. The ratio of **4**:**5** was shown not to depend on the method of decomposition of **1** and had a value of 0.66 ± 0.2. The relative amounts of olefins **4** and **5**, which result from hydrogen migration, and **8**, which results from phenyl migration, varied with the mode of decomposition and with temperature. Thermal and photochemical decomposition of 2,2-diphenyldiazopropane (**10**) produced the same ratio of (*Z*)-/(*E*)-1,2-diphenylpropenes as from **1**. These data are shown to be consistent with a mechanism involving production of the carbene (**2**) from diazo compound **1**. The two carbene spin states, singlet and triplet, are postulated to be interconverting, and it is the singlet state which gives rise to hydrogen rearrangement while the triplet allows phenyl migration. The observation of two different carbenes (**2** from **1** and **11** from **10**) giving rise to the same olefin ratio (**4**/**5**) by migration of different groups argues for the existence of a discrete intermediate in the conversion of these carbenes (**2** and **11**) to olefins **4** and **5**. It is suggested that this intermediate might best be formulated as the phantom singlet state (**3**) of $\alpha$-methylstilbene. An additional study involving 1-(*p*-phenyl-*d*)-2-phenyldiazopropane (**9**) has reconfirmed the migratory aptitude sequence to a carbene center as $H > Ph > CH_3$.

The photochemical and photosensitized interconversions of *E* and *Z* olefin pairs have been the object of considerable study over the past years. In 1964, in a now classic paper, Hammond postulated that the photosensitized isomerization of the stilbenes involved the formation of an intermediate having an energy close to that of the *E* triplet while similar isomerizations of the 1,2-diphenylpropenes involved an intermediate whose energy was significantly lower than that of the *E* triplet.[4] They postulated that the geometry of this state was one in which the groups around the original double bond were now twisted by 90° (Figure 1) and termed this state the phantom triplet. Further studies[4] led them to propose that the direct isomerization of the olefins also went by way of the triplet state and involved the phantom triplet. By employing high-energy photosensitizers he was able to show that this phantom triplet, whether formed from the direct or sensitized isomerization, led to a single "decay ratio" for a particular olefin pair. Thus the *Z*/*E* ratio for the stilbenes produced from the phantom triplet was 1.5 and for the 1,2-diphenylpropenes it was 1.2.

Recently Saltiel and coworkers[5] demonstrated that the quenching of the direct isomerization of the stilbenes by azulene was considerably more pronounced in the sensitized reaction than in the unsensitized one. He thus concluded that the direct photochemical isomerization of stilbene proceeds *via* the singlet state and involves the phantom singlet which has about the same decay ratio (1.3 in benzene solution) as the phantom triplet (1.4 in benzene solution).[6,7] 1,2-Diphenylpropene did not show a comparable azulene effect on the sensitized isomerization and so could not be similarly studied.

We therefore deemed it desirable to attempt to prepare this phantom state independent of the olefin precursors and to measure its decay to the *E* and *Z* olefins. It was also hoped that this could be done in both the singlet and triplet states. We chose to examine the thermal, direct photochemical, and photosensitized decomposition of 1,2-diphenyl-1-diazopropane (**1**). It was anticipated that the carbene, **2**, would be the intermediate in these reactions since it is well known that such decompositions produce carbenes.[8] In addition, singlet carbenes are produced by thermal and direct photochemical decomposition and triplet carbenes by photosensitized decomposition.[8] It should be pointed out that in the former two cases the product ratios are often somewhat different indicating either differences in energy content of the carbenes or that some of the observed reactions are concerted.

Migration of a hydrogen[9] would result in rehybridization of the original quarternary carbon to sp$^2$ and final hybridization of the carbenic carbon also would be sp$^2$ since this is the hybridization in the product. Least motion considerations would suggest the phantom

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[2] Visiting Professor, The University of Wisconsin, Madison, Wis., Fall 1972. M. P. wishes to thank the Chemistry Department of the University of Wisconsin for their kind hospitality.

[3] This work was taken from the Ph.D. Thesis of T. H. Witherup, Case Western Reserve University, 1972; presented in part at Metrochem 72 Fairleigh Dickinson University, Teaneck, N. J., May 1972, and at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, ORGN-107.

[4] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964); W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966); D. H. Valentine, Jr., and G. S. Hammond, *ibid.*, **94**, 3449 (1972).

[5] J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafiriou, paper presented at the Symposium on Frontiers in Organic Photochemistry, Tarrytown, N. Y., Oct 1970.

[6] J. Saltiel and E. D. Megarity, *J. Amer. Chem. Soc.*, **94**, 2742 (1972); J. Saltiel and J. T. D'Agostino, *ibid.*, **94**, 6445 (1972).

[7] See, however, S. Sharafy and K. A. Muszkat, *ibid.*, **93**, 4119 (1971), and references therein.

[8] W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971, pp 18–29.

[9] W. Kirmse, ref 8, p 236 ff.

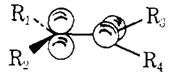
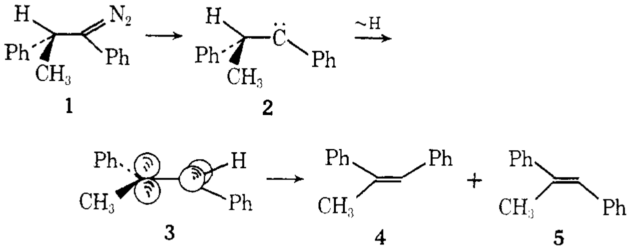


Figure 1.

state as the intermediate. Of course, the alternative would be concerted production of the olefins directly from the carbene as has been suggested by Zimmerman[10,11] based on orbital following considerations, and by Dewar[12] based on MINDO/2 calculations. Scheme I depicts the hoped-for pathway. It was also anticipated that since carbene, **2**, could be produced in both spin states **3** might also be formed in both states.

**Scheme I**



In studies on $\beta$-alkoxycarbenes,[13] an $\alpha,\beta$-dicarboalkoxycarbene,[14] alkylcarbenes,[14] and $\alpha,\beta$-diphenylethylidene[14] it was concluded that steric and electronic factors control the hydrogen (or alkyl group) migration from $C_\beta$ to $C_\alpha$. Thus the conformation shown in Figure 2 will produce the olefin with A and B cis to each other. The relative populations of the conformers of the carbene will determine the ratio of *E/Z* olefins produced. If group C is repelled by the nonbonding electron pair on the carbenic center (Figure 2) the predominant olefin will have A and B cis to each other. Also if B and D are large groups and crowd one another then again the olefin having A and B cis will predominate. In these studies[13,14] no mention was made about the possibility of a single intermediate phantom state (or similar species) being formed and this decaying to ground-state olefins.

It should also be mentioned that 1,2-alkyl and hydrogen migrations in carbenes undoubtedly go through the singlet state (the migration to an empty p orbital is allowed by orbital symmetry), whereas a phenyl group can migrate in the triplet state (orbital symmetry allowed radical 1,2-phenyl migration using the $\pi$ system of the phenyl ring)[11-18] as well as the singlet state.

## Results

**1,2-Diphenyl-1-diazopropane (1).** 1,2-Diphenyldiazopropane (**1**) was prepared by the oxidation of the hydrazone of $\alpha$-phenylpropiophenone by yellow mercury(II) oxide. The complete synthetic route, starting from 2-phenylpropionaldehyde, is shown in Scheme II.

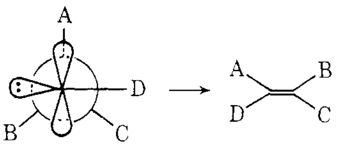
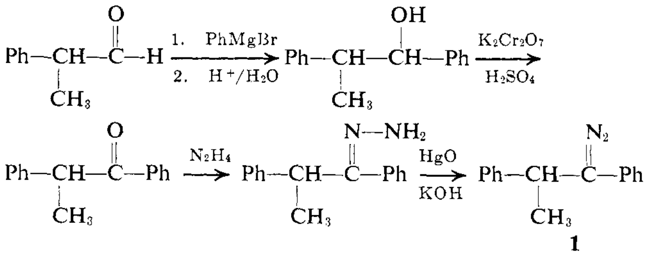


Figure 2.

**Scheme II**



$$\mathrm{Ph{-}\underset{CH_3}{CH}{-}\overset{O}{\overset{\|}{C}}{-}H \xrightarrow[2.\ H^+/H_2O]{1.\ PhMgBr} Ph{-}\underset{CH_3}{CH}{-}\overset{OH}{CH}{-}Ph \xrightarrow[H_2SO_4]{K_2Cr_2O_7}}$$

$$\mathrm{Ph{-}\underset{CH_3}{CH}{-}\overset{O}{\overset{\|}{C}}{-}Ph \xrightarrow{N_2H_4} Ph{-}\underset{CH_3}{CH}{-}\overset{N{-}NH_2}{\overset{\|}{C}}{-}Ph \xrightarrow[KOH]{HgO} Ph{-}\underset{CH_3}{CH}{-}\overset{N_2}{\overset{\|}{C}}{-}Ph}$$

**1**

The diazo compound was a dark red oil which could not be crystallized. It had the following spectral characteristics: nmr $\tau$ 2.95 (m, 10, Ar*H*), 6.15 (q, 1, $J$ = 7.1 Hz, C*H*CH$_3$), and 8.52 ppm (d, 3, $J$ = 7.1 Hz, CHC*H*$_3$); ir 4.92 $\mu$ (2033 cm$^{-1}$), very strong, $C{=}N^+{=}N^-$;[19] vis–uv $\lambda_{max}^{benzene}$ 516 nm ($\epsilon$ 36); $\lambda_{max}^{hexane}$ 286 nm ($\epsilon$ $2.0 \times 10^4$). The yield of **1** was always greater than 95% as shown by nmr spectroscopy and the major impurity was the ketone, $\alpha$-phenylpropiophenone, which was absent in the hydrazone. The amount of this ketone could be kept to a minimum by carrying the oxidation and isolation out under nitrogen, which suggests the ketone arose by reaction with atmospheric oxygen.

Although **1** was stable in solution at 0° for several weeks, it was used within a short time after it was prepared.

In order to examine the starting material (**1**) for olefins, and to run some decompositions to partial completion, it was necessary to destroy the excess diazo compound without producing the olefins. We found that dimethyl acetylenedicarboxylate reacted rapidly and efficiently with the diazo compound (**1**) without producing any (*Z*)- or (*E*)-1,2-diphenylpropenes (**4** or **5**). Addition of a known mixture of **4** and **5** to the diazo solution prior to quenching produced no change in composition after reaction with dimethyl acetylenedicarboxylate. Only trace amounts of these olefins were present in the starting diazo solutions. We did not unequivocally identify the product of these quenching reactions although the nmr and mass spectra were consistent with a 1,3-dipolar addition product.[20]

**Thermal Decomposition of 1,2-Diphenyldiazopropane (1).** Thermal decompositions of the diazo compound (**1**) were run initially by slowly adding a ($10^{-2}$ *M*) solution of **1** in an appropriate solvent to the same solvent heated to reflux. The flask was shielded from stray light and the reaction color went from red to orange to bright yellow. A second procedure was also used which

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[10] H. E. Zimmerman and L. R. Sousa, *J. Amer. Chem. Soc.*, **94**, 834 (1972).

[11] H. E. Zimmerman, *Accounts Chem. Res.*, **5**, 393 (1972).

[12] N. Bodor and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **94**, 9103 (1972).

[13] W. Kirmse and M. Buschoff, *Chem. Ber.*, **100**, 1491 (1967).

[14] Y. Yamamoto and I. Moritani, *Tetrahedron*, **26**, 1235 (1970).

[15] I. Moritani, Y. Yamamoto, and S. I. Murahashi, *Tetrahedron Lett.*, 5697, 5755 (1968).

[16] See also, M. Jones, Jr., and W. Ando, *J. Amer. Chem. Soc.*, **90**, 2200 (1968); H. E. Zimmerman and J. H. Munch, *ibid.*, **90**, 187 (1968).

[17] M. B. Sohn and M. Jones, Jr., *ibid.*, **94**, 8280 (1972); M. Jones, Jr., private communication.

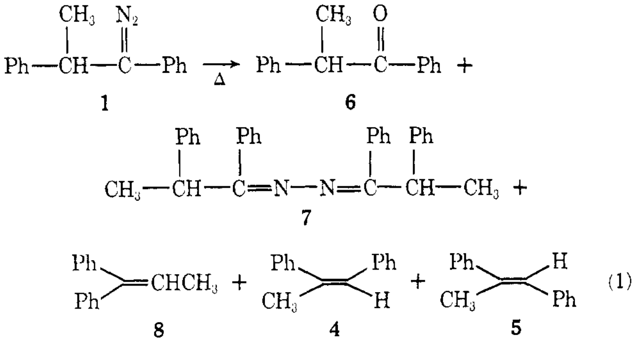
[18] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

[19] G. W. Cowell and A. Ledwith, *Quart. Rev., Chem. Soc.*, **24**, 119 (1970).

[20] See, *e.g.*, R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565, 633 (1963); R. A. Firestone, *J. Org. Chem.*, **33**, 2285 (1968); R. Huisgen, *ibid.*, **33**, 2291 (1968); L. C. Behr, R. Fusco, and C. H. Jarboe, "Pyrazoles, Pyrazolines, Pyrazolidines, Indazoles and Condensed Rings," R. H. Wiley, Ed., "The Chemistry of Heterocyclic Compounds," Vol. 22, A. Weissberger, Ed., Wiley, New York, N. Y., 1967.

involved sealing a solution of **1** in benzene (*ca.* $10^{-2}$ *M*) in a Pyrex ampoule, shielded from stray light, and immersing this in a thermostated bath.

In order to identify the products of the decomposition several runs were combined. Vlpc, column chromatography, and nmr analysis indicated five major components: α-phenylpropiophenone (**6**), α-phenylpropiophenone azine (**7**), 1,1-diphenylpropene (**8**), (*Z*)-1,2-diphenylpropene (**4**), and (*E*)-1,2-diphenylpropene (**5**; eq 1). The olefins **4**,[21] **5**,[21] and **8**[21e,22] and the ketone (**6**)[23] were identified by spectral comparison with authentic compounds. Alumina column chromatography separated **4**, **5**, **6**, and **8** from a yellow oil which appeared to be the azine, **7**, present as a mixture of isomers. We prepared this azine from the ketone (**6**) and its hydrazone using the method of Overberger.[24] The synthesized material displayed the same nmr patterns, coupling constants, and chemical shift ranges (doublets at *ca.* τ 8.5 ppm and quartets at *ca.* τ 5 ppm; ratio = 3:1) as that of the yellow oil (although peak ratios were slightly different) and therefore the azine, **7**, is concluded to be a product from the diazo decomposition.



In a large scale thermal decomposition in benzene (75°), nmr analysis indicated that the azine yield was *ca.* 20% although the amount varied with temperature. In addition, the yield of (*Z*)-1,2-diphenylpropene (**4**), (*E*)-1,2-diphenylpropene (**5**), and 1,1-diphenylpropene (**8**) combined was *ca.* 50% and α-phenylpropiophenone (**6**) was *ca.* 30%.

Table I lists the data obtained using refluxing solvents for the ratio of (*Z*)-/(*E*)-1,2-diphenylpropene (**4**:**5**) as well as the ratio of hydrogen shifted product (**4** + **5**) to phenyl migrated product (**8**). It should be pointed out that the decompositions were run several times and, since the analysis was by vlpc, several chromatograms were taken for each run. Vlpc was shown not to interconvert the olefins; the areas were obtained by triangulation (half-height method) and, for the olefins, it was demonstrated that no correction was necessary for differences in flame ionization detector response.

**Table I.** Thermal Decomposition of **1** in Refluxing Solvent

| Solvent | Temp, °C | **4**:**5** | (**4** + **5**):**8** |
|---|---|---|---|
| Benzene | 80 | 0.87 | 7.1 |
| Toluene | 110 | 0.67 | 4.9 |
| Xylene | 144 | 0.68 | 8.0 |
| Mesitylene | 165 | 0.63 | 7.3 |
| | | Av 0.71 ± 0.16 | 6.8 |

Table II shows typical data for the decompositons (all in benzene) at various temperatures using sealed ampoules in a thermostated bath. Once again the data in the table represent the average of a large number of runs. Thus the data of Tables I and II indicate that the ratio of **4**:**5** is 0.66 ± 0.2 and the (**4** + **5**):**8** ratio is about 5.5 ± 2.

**Table II.** Sealed Ampoule Decomposition of **1** in Benzene

| Temp, °C (±0.3°) | **4**:**5** | (**4** + **5**):**8** |
|---|---|---|
| 75.0 | 0.73 | 3.7 |
| 100.0 | 0.58 | 3.9 |
| 125.0 | 0.52 | 4.0 |
| 150.0 | 0.56 | 4.8 |
| | Av 0.60 ± 0.15 | 4.1 |

The large scatter in the experimental data was studied and the possible sources of these deviations were examined. Although, as will be discussed below, we looked at a large number of possibilities, we were unable to find the source of this scatter.

We were able to eliminate glass surface catalysis as the culprit by carrying out the reaction in the presence of powdered Pyrex. Prereaction treatment of the tubes with acid (HCl solution), base ($NH_3$ solution), or distilled water did not improve the numbers. Variations in concentration and the volume of the tubes had no effect. The presence of oxygen did not affect the **4**:**5** ratio appreciably although the amount of ketone (**6**) increased significantly. It was also found that bubbling oxygen through the diazo solution at room temperature did not produce the ketone (**6**) as evidenced by nmr spectroscopy. In addition, the method of degassing likewise had no effect.

We next considered acid and water catalysis even though our solvents had been dried and stored over "Dri Na." When the decomposition was run at two different temperatures in the presence of excess water, the ratio seemed to have increased a small amount but was still within the experimental error limits of 0.66 ± 0.2.

Acid-catalyzed decomposition of the diazo compound (**1**) at room temperature produced significantly more of the *Z* isomer (**4**) than the *E* isomer (**5**). Thus we can rule out acid-catalyzed decomposition as being the source of the experimental error. Table III lists the acid-catalyzed decomposition results.

**Table III.** Acid-Catalyzed Decomposition of **1**

| Acid | **4**:**5** | Acid | **4**:**5** |
|---|---|---|---|
| $BCl_3$ | 9.8 | Alumina | 1.8 |
| HOAC | 7.4 | CuCl | 1.4 |
| HCl | ~4 | | |

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(21) (a) D. J. Cram and F. A. Abd Elhafez, *J. Amer. Chem. Soc.*, **74**, 5851 (1952); (b) F. A. Abd Elhafez and D. J. Cram, *ibid.*, **75**, 339 (1953); (c) D. H. Hunter and D. J. Cram, *ibid.*, **86**, 5478 (1964); (d) J. H. Brewster and H. O. Bayer, *J. Org. Chem.*, **29**, 105 (1964); (e) V. J. Traynelis, W. L. Hergenruther, J. R. Livingston, and J. A. Valicenti, *ibid.*, **27** 2377 (1962).

(22) C. Hell and H. Bauer, *Ber.*, 37, 230 (1904).

(23) H. Christol, A. Laurent, and G. Solladie, *Bull. Soc. Chim. Fr.*, 877 (1963).

(24) C. G. Overberger and H. Gainer, *J. Amer. Chem. Soc.*, **80**, 4556 (1958).

Decomposition of **1** at 75° in the presence of benzoyl peroxide did not affect the **4**:**5** ratio as did the use of the inhibitor di-*tert*-butyl nitroxide.

**Photochemical Decomposition of 1,2-Diphenyldiazopropane (1).** The photochemical decomposition of **1** gave more reproducible $Z/E$ ratios than the thermal reactions with very little or no azine being formed. In order to avoid product isomerization, we used filters as follows. Filter A was cupric sulfate–sodium nitrite[25] with a maximum transmittance at 420 nm, filter B was cupric chloride–calcium chloride[25] with a maximum transmittance at 533 nm, and filter C was a Coleman Instrument Corp. no. PC-1 glass filter with a cut-off (absorbance >2.0) at 400 nm. Table IV lists the results, all at room temperature (15–20°). All **4**:**5** ratios, once again, are within the 0.66 ± 0.2 range for thermal decompositions. The hydrogen to phenyl rearrangement product ratio is now 1.9–2.0 (down from the thermal ratio) and the heavy atom solvent is lower by what we consider to be outside of the experimental error. The nature of this heavy atom effect will be discussed later.

**Table IV.** Photochemical Decomposition of **1**

| Solvent | Filter | **4**:**5** | (**4** + **5**):**8** |
|---|---|---|---|
| Benzene | A | 0.83 | 2.0 |
| Benzene | B | 0.78 | 1.9 |
| Benzene | C | 0.86 | 1.9 |
| Bromobenzene | A | 0.68 | 1.7 |

Control experiments indicated that the olefins did not rearrange under the reaction conditions. The diazo compound was shown not to be sensitizing olefin isomerization by irradiating **1** (with a filter) in the presence of *trans*-stilbene and not observing any *cis*-stilbene. Similarly, sensitization by the ketone (**6**) and the azine (**7**) were ruled out.

**Photosensitized Decomposition of 1,2-Diphenyldiazopropane (1).** For reasons of solubility (benzene solvent) and wavelength (irradiation at a wavelength where the diazo compound had a minimal absorption) we chose benzil and fluorenone as sensitizers. They both have $\lambda_{\mathrm{max}}$ close to 400 nm (near the minimum in the absorption spectrum of **1**), fairly high triplet energies ($E_{\mathrm{T}}$ = 53–54 kcal/mol), and high intersystem crossing quantum yields ($\Phi_{\mathrm{ISC}}$ = 0.92–0.93).[26]

In order to ensure that the product olefins were not undergoing sensitized isomerization, the decompositions were carried to about 10–20% completion. The excess diazo compound was destroyed using dimethyl acetylenedicarboxylate as discussed above, and a correction was made for the small amount of olefins present in the diazo compound. This was only significant at less than about 5% reaction. We also were able to demonstrate, by monitoring the $Z/E$ ratio as a function of per cent decomposition, that up to about 20% reaction, using fluorenone as sensitizer, the ratio was essentially invariant but above 20% began to increase toward the photostationary state value for this sensitizer.[4] The extent of decomposition of **1** was monitored by visible spectroscopy and the reaction was also carried out at room temperature.

**Table V.** Photosensitized Decomposition of **1**

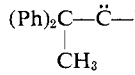
| Sensitizer | **4**:**5** | (**4** + **5**):**8** |
|---|---|---|
| Fluorenone | 0.68 | 1.4 |
| Benzil | 0.51 | 1.4 |

Table V shows the sensitization results including the (**4** + **5**):**8** ratio. Once again the ratio of (*E*)- to (*Z*)-$\alpha$-methylstilbene is within the value of 0.66 ± 0.2. In addition, the amount of phenyl migration has increased significantly.

**1-(*p*-Phenyl-*d*)-2-phenyldiazopropane (9).** The olefins **4** and **5** could be arising from carbene **2** by either a hydrogen or a methyl migration. If **3** is indeed the intermediate then the $Z/E$ (**4**:**5**) ratio must be the same from methyl as from hydrogen migration. To check whether there indeed was methyl migration and whether the ratio was the same, we prepared 1-(*p*-phenyl-*d*)-2-phenyldiazopropane (**9**) by the same route as for **1** except that *p*-phenyl-*d*-magnesium chloride was employed. This was prepared by reacting *p*-bromochlorobenzene with magnesium in ether followed by reaction with $D_2O$ to produce *p*-chlorobenzene-*d*. This was converted to the Grignard reagent by reaction with magnesium in THF. The chlorobenzene-*d* and the ketone precursor of **9** were both shown by mass spectroscopy to contain 94% of one deuteron.

Thermal (100°) and direct photochemical (filter A, $\lambda_{\mathrm{max}}$ 420 nm) decomposition of **9** were followed by vlpc separation and collection of the *Z* and *E* olefins, **4** and **5**. Ozonolysis and mass spectral analysis of the acetophenone produced showed less than 1% of deuterium; *i.e.*, less than 1% methyl migration had occurred. This result, taken with the observation of more hydrogen migration in the carbene than phenyl migration, confirms the known[27] migratory aptitudes of H > $C_6H_5$ > $CH_3$ to a carbenic center.

**2,2-Diphenyl-1-diazopropane (10).** We next turned to the preparation of 2,2-diphenyl-1-diazopropane (**10**) with the anticipation that it would produce carbene **11** on decomposition followed, at least in part, by rearrangement of a phenyl group, once again, to the same phantom intermediate **3**. The ratio of (*Z*)-/(*E*)-$\alpha$-methylstilbenes (**4** and **5**) so obtained could be compared to the value of 0.66 ± 0.2 observed from rearrangement of the isomeric carbene **2**.

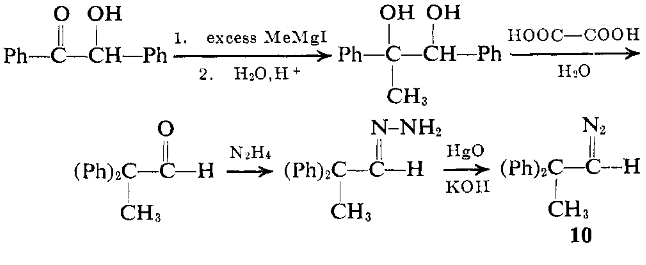


$$(\mathrm{Ph})_2\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{C}}-\ddot{\mathrm{C}}-\mathrm{H}$$

**11**

Scheme III shows the synthetic route to **10**. Re-

**Scheme III**



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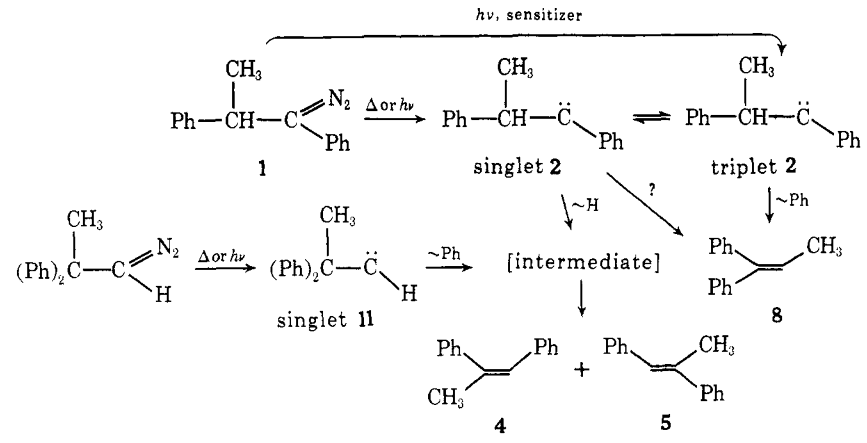
(25) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1967, Chapter 7.

(26) Reference 25, Chapter 4.

(27) H. Philip and J. Keating, *Tetrahedron Lett.*, 523 (1961).

**Scheme IV**



action of somewhat more than 2 equiv of methylmagnesium iodide with benzoin followed by hydrolysis produced 1,2-diphenyl-1,2-propanediol[28] which was allowed to rearrange on treatment with aqueous oxalic acid to 2,2-diphenylpropanal.[29] The hydrazone, which turned out to be a liquid, was prepared in the usual way.[30] Mercury(II) oxide oxidation of the hydrazone produced 2,2-diphenyl-1-diazopropane (**10**) which was observed to be unstable at room temperature. As a result the studies were made on "freshly prepared" material which had only decomposed to a small extent.

Table VI shows the results of decomposing **10** thermally at room temperature and at 100° and photochemically at room temperature using filter A (420 nm). It is thus apparent that the (*Z*)-:(*E*)-α-methylstilbene (**4**:**5**) ratio is very close to the 0.66 value for 1,2-diphenyl-1-diazopropane (**1**) decompositions. It should also be mentioned that some methyl migration was occurring since there was about 16% (relative to **4** + **5**) of 1,1-diphenyl-1-propene (**8**) among the products.

**Table VI.** Decomposition of 2,2-Diphenyl-1-diazopropane (**10**)

| Method | **4**:**5** |
|---|---|
| Spontaneous (thermal, 25°) | 0.70 |
| Thermal (100°) | 0.65 |
| Photolysis (filter A, 20°) | 0.57 |

We were also able to rule out catalytic decomposition of the diazo compound (**10**) by mercury(II) oxide in the following way. First we used $MnO_2$ as the hydrazone oxidant to prepare the diazo compound (**10**). This resulted in a more rapid decomposition of **10** during its preparation. In addition, $MnO_2$ rapidly decomposed both diazo compound **1** and diazomethane. In contrast, no decomposition of **10** or diazomethane was observed when mercuric oxide was added to these species. Thus it is most reasonable to assume that **10**, like the other two diazo compounds studied, is stable to mercuric oxide and that the room temperature decomposition is a truly thermal reaction.

## Discussion

The most reasonable mechanism consistent with the data involves a single precursor for the two olefins, (*Z*)- and (*E*)-α-methylstilbene (**4** and **5**). This follows since the same olefin ratio is not only obtained by decomposing diazo compound **1** thermally, photochemically, and by photosensitization but also by decomposing **10** thermally and photochemically. It has often been assumed that the conversion of a carbene to an olefin by intramolecular insertion into an adjacent C–H bond is a concerted process.[10–14] In fact, the molecular orbital following approach of Zimmerman[10,11] predicts that the concerted rearrangement from carbene to olefin is the allowed reaction whereas a stepwise process is forbidden.

It would have to be rather fortuitous for two totally dissimilar carbenes (**2** and **11**; one containing a conjugating phenyl ring (**2**) and the other not) to rearrange by migration of very different groups (hydrogen in **2** and phenyl in **11**) and give the same ratio of olefins by a concerted process. We believe, therefore, that it is more reasonable to consider the reaction of this carbene to olefins as involving a discrete intermediate which has a set of properties (decay ratio to *Z* and *E* olefins) independent of its genesis.

The geometry of this intermediate is subject to speculation but its electronic nature can be established by the experiments presented above. It is well known that hydrogen migration occurs from the singlet state of the carbene and, by analogy with free radicals, a phenyl group can migrate in the triplet state.[10–18] The mechanism for the overall reaction of 1,2-diphenyldiazopropane (**1**) can be envisioned as shown in Scheme IV. Thermal and photochemical decomposition of **1** gives the singlet carbene initially while sensitized decomposition produces the triplet state. Depending on the conditions, these two carbene electronic states can, since we are dealing with phenylcarbenes, at least interconvert if not come to equilibrium.[15,17,31] The singlet carbene can then form an intermediate by hydrogen migration which is the progenitor of **4** and **5** and is also of singlet multiplicity. In addition, phenyl migration in singlet **2** can produce 1,1-diphenyl-1-propene (**8**) but this is not required by the mechanism. The triplet carbene can migrate a phenyl group to produce **8**. Since the relative rates of reaction of

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(28) M. Tiffeneau and H. Dorlencourt, *Ann. Chim. Phys.*, [8] **16**, 237 (1909); *Chem. Zentralbl.*, **80**, 1335 (1909).

(29) J. Lévy, *Bull. Soc. Chim. Fr.*, **29**, 865 (1921).

(30) L. I. Smith and K. L. Howard, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 351; J. B. Miller, *J. Org. Chem.*, **24**, 560 (1959).

(31) T. A. Baer and C. D. Gutsche, *J. Amer. Chem. Soc.*, **93**, 5180 (1971); R. A. Moss and U. H. Dolling, *ibid.*, **93**, 954 (1971); G. L. Closs, *Top. Stereochem.*, **3**, 193 (1968).

singlet and triplet carbenes are most likely temperature dependent and since the triplet state is undoubtedly of lower energy than the singlet state[32] higher temperatures might favor singlet reactions while lower temperatures might favor triplet ones. In addition, reaction through the singlet should be favored when the singlet is produced initially, while reaction through the triplet should be favored when it is formed initially. That is to say the two spin states are not necessarily in equilibrium. The observation of a single decay ratio for production of the *Z* and *E* olefins **4** and **5** and the dependence of the (**4** + **5**):**8** ratio on whether high temperatures (75–150°) or lower temperatures (20°) were employed supports this contention. Thus the singlet carbene produced initially by thermal and direct photochemical decomposition of the diazo compound (**1**) gives more hydrogen migration relative to phenyl migration at higher temperatures ((**4** + **5**):**8** = 5.5) than at lower temperatures ((**4** + **5**):**8** = 2.0). When the triplet carbene is initially produced by sensitized decomposition then the amount of phenyl migration increases relative to hydrogen shift ((**4** + **5**):**8** = 1.4). In addition, the use of a heavy atom solvent, bromobenzene, to enhance the intersystem crossing of the singlet to the triplet carbene[33] resulted in somewhat greater phenyl migration ((**4** + **5**):**8** = 1.7) in a direct photochemical decomposition at 20°. Thus the data are totally consistent, at least qualitatively, with the mechanism shown in Scheme IV.

The nature of the singlet intermediate cannot be established unequivocally from the data. One interpretation would formulate it as the photochemical "phantom" singlet where the groups around the "double" bond are perpendicular. This would be the case if the direct isomerization of **4** and **5** went *via* the triplet state as originally postulated by Hammond.[4] His decay ratio (**4**:**5**) was observed to be 1.2 whereas ours is 0.66 ± 0.2. This is supported by the work of Muszkat and Fischer, *et al.*,[7] who contend that stilbene direct isomerization goes *via* the triplet state. The diphenylpropenes (**4** and **5**) would be expected to be similar.

If, on the other hand, the direct stilbene isomerization involves the singlet state as postulated by Saltiel,[6] then similar behavior by the diphenylpropenes would require that the intermediate observed in our work not be the "phantom" singlet which lies on the photochemical potential energy surface. Instead the intermediate would probably lie on the thermal potential energy surface but still might have the geometry of the phantom state. It could, under these circumstances, be an energy minimum in a shallow well on the thermal surface connecting the *E* and *Z* isomers. If this latter is true then it follows that the decay ratios obtained in the photochemical studies are determined, at least partially, by something other than crossing of the phantom photochemical singlet to the phantom thermal singlet.

It is also worth speculating that since the conversion of either phantom singlet to the olefins is a highly exothermic reaction one might have expected less selectivity in the **4**:**5** ratio (*i.e.*, a number closer to unity). The greater selectivity can be rationalized in the following way. The formation of the phantom singlet (**3**) from the carbene **2** must be exothermic by about 18 kcal/mol and the formation of olefins from the phantom singlet must be exothermic by approximately a further 40 kcal/mol.[34] The 18 kcal/mol is obtained by first calculating $\Delta H_f°$ for the phantom state of ethylene as 72 kcal/mol from the equation

$$CH_3{-}CH_3 \longrightarrow \dot{C}H_2{-}\dot{C}H_2 + 2H$$

and $\Delta H_f°$ ($C_2H_6$) = −20.2 kcal/mol,[35] $\Delta H_f°$ (H·) = 52.1 kcal/mol,[35] and with DH° ($CH_3CH_2$–H) as 98 kcal/mol.[36] $\Delta H_f°$ of ethylidene is obtained as 77 kcal/mol from the $\Delta H°$ for the following equation

$$CH_3\cdot \longrightarrow H\cdot + CH_2{:}$$

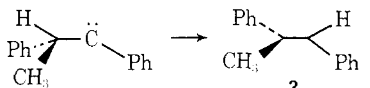
Using $\Delta H_f°$ ($CH_3\cdot$) = 34 kcal/mol,[36] $\Delta H_f°$ ($CH_2$:) = 92 kcal/mol,[37] and $\Delta H_f°$ (H·) = 52.1 kcal/mol then $\Delta H°$ = 110 kcal/mol. Now, since the addition of a methyl group lowers the dissociation energy of the C–H bond by 6 kcal/mol (DH° ($CH_3$–H) = 104 kcal/mol and DH° ($CH_3CH_2$–H) = 98 kcal/mol) then for the reaction

$$CH_3{-}CH_2\cdot \longrightarrow H\cdot + CH_3{-}\ddot{C}H$$

$\Delta H°$ would be estimated as 110 − 6 = 104 kcal/mol. This gives the $\Delta H_f°$ ($CH_3CH$:) = 77 kcal/mol using $\Delta H_f°$ ($CH_3CH_2\cdot$) = 25 kcal/mol.[36]

Thus the conversion of ethylidene to the phantom state of ethylene should be exothermic by approximately 5 kcal/mol.

If we assume that $\Delta H°$ for the conversion of **2** to **3** is the same 5 kcal/mol corrected for the conjugation effects of the phenyl rings then we can calculate an approximate exothermicity for the reaction



2 3

of about 18 kcal/mol. If we assume the phenyl ring in **2** conjugates with one electron, as it would in the lower energy triplet, and the two phenyl rings in **3** each conjugate with an electron then **3** gains an additional 13 kcal/mol stabilization, that is, the value for the stabilization energy of one benzylic radical.[35]

An alternative calculation uses the estimated bond energies reported by Dewar[38] based on bond strength–hybridization correlations. The carbene, ethylidene, with 3 sp$^3$ C–H bonds, one approximately sp$^2$ C–H bond, and one sp$^3$–sp$^2$ C–C bond, has a total bond energy of (3 × 97 + 1 × 100.5 + 1 × 89.6) 481 kcal/mol. The phantom state of ethylene has a total bond energy of [4 × 100.5 (sp$^2$ C–H) + 95.0 (sp$^2$–sp$^2$ C–C)] 497 kcal/mol. The conversion of ethylidene to the phantom state of ethylene is therefore calculated to be exothermic by 16 kcal/mol. Thus the formation of the phantom state **3** from carbene **2** would be exothermic by 28 kcal/mol.

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[32] A. M. Trozzolo, *Accounts Chem. Res.*, 1, 329 (1968).

[33] See, *e.g.*, N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 50.

[34] $E_{act}$ for stilbene isomerization is 43 kcal/mol in the gas phase and 38 kcal/mol in solution: G. B. Kistiakowsky and W. R. Smith, *J. Amer. Chem. Soc.*, **56**, 638 (1934); T. W. T. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938).

[35] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

[36] D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

[37] W. A. Chupka and C. Lifshitz, *J. Chem. Phys.*, **48**, 1109 (1968); W. A. Chupka, *ibid.*, **48**, 2337 (1968).

[38] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **11**, 96 (1960).

These crude calculations indicate a significant exothermicity from carbene (**2**) to phantom state (**3**) and so this state must initially have excess vibrational energy. It is difficult to see why an energetic species, even after vibrational deactivation, should not give roughly equal amounts of the two isomeric olefins but should give about twice as much of the more stable one and thus reflect, to a significant extent, the relative ground-state stabilities. Because of a lack of relevant data we will not speculate at this time on the exact nature of the decay process although several highly speculative alternatives can be conceived.

## Experimental Section

Melting points and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 237 or 700 or a Beckman IR-8 spectrometer using either neat samples in sodium chloride sandwich cells or in $\text{CCl}_4$ solution in 0.1-mm cells. Visible and ultraviolet spectra were obtained on a Cary 15 or Hitachi Perkin-Elmer 139 UV-VIS spectrometer. Nmr spectra were recorded on Varian A-60 or A-60A spectrometers equipped with a C-1024 time-averaging computer[39] and a V-6058A spin decoupler. Unless otherwise specified, 10–20% solutions in $\text{CCl}_4$ containing 2% TMS were used for the nmr spectra. Mass spectra were obtained on a JEOL-07 spectrometer.

Vapor phase chromatography was performed on either a flame ionization detector instrument using 0.125-in. columns or a thermal conductivity detector instrument using 0.25-in. columns. The following columns were employed: (A) 15 ft × 0.125 in. 2% triisodecyl trimellitate (Morflex 530) on 80–100 mesh Aeropak 30; (B) 11 ft × 0.125 in. 2% Morflex 530 on 80–100 mesh Aeropak 30; (C) 9 ft × 0.125 in. 2% Morflex 530 on 80–100 mesh Aeropak 30; (D) 5 ft × 0.25 in. 10% Carbowax 20M on 45–60 mesh Chromosorb P; (E) 5 ft × 0.25 in. 5% SE-30 on 45–60 mesh Chromosorb P; (F) 3 ft × 0.25 in. 10% Carbowax 20M on 60–80 mesh Chromosorb P; (G) 4 ft × 0.25 in. 2% DC 710 silicone oil on 80–100 mesh Aeropak 30.

Vlpc peak areas were measured by triangulation (half-height method) since it was found to be the most reliable procedure. Relative FID response factors were determined for the olefins **4**, **5**, and **8** and the ketone **6**. For the olefins these factors were within experimental error of 1.00.

**Syntheses. 1,2-Diphenyl-1-propanol.**[23] To a solution of phenylmagnesium bromide prepared from 9.6 g (0.4 g-atom) of magnesium and 59 g (0.38 mol) of bromobenzene in 65 ml of ether in a 1-l. three-necked flask equipped with a condenser and drying tube, addition funnel, gas inlet, thermometer, and magnetic stirrer was added a solution of 2-phenylpropionaldehyde (41 g, 0.30 mol) in 50 ml of ether. The flask was cooled with an ice bath such that the temperature was maintained at *ca.* 10° and the reaction mixture was kept under $\text{N}_2$ and stirred. After the addition, the mixture was refluxed for 1 hr, cooled, and ice and 200 ml of 10% HCl were added slowly. The layers were separated, the aqueous layer was extracted twice with ether, and the combined ether solution was washed with $\text{NaHCO}_3$ solution, water, and NaCl solution and dried over $\text{MgSO}_4$. Filtration followed by rotary evaporation produced 60 g (94%) of crude alcohol as a light yellow oil. It was found that purification for further reaction was unnecessary although some samples were distilled: bp 140–145° (42 mm); nmr $\tau$ 2.9 (m, 14 Ar*H*), 5.5 (d, 1, $J$ = 6.1 Hz, C*H*OH), 7.1 (m, 1, C*H*CH$_3$), 7.5 (s, 1, OH), 8.8 ppm (d, 3, $J$ = 7.0 Hz, CHC*H*$_3$).

**1,2-Diphenylpropanone (6).**[23] To 42 g (0.2 mol) of 1,2-diphenyl-1-propanol in a 500-ml three-necked flask equipped with a thermometer, stirrer, condenser, and addition funnel was added an acid solution consisting of 80 g (0.27 mol) of potassium dichromate, 120 g (1.2 mol) of concentrated sulfuric acid, and 160 ml of water. The addition was such that the temperature did not rise above 70° and after the addition this temperature was maintained for an additional hour. The reaction mixture was cooled to 0° and extracted with ether. The ether extract was washed with water, $\text{NaHCO}_3$, water, and NaCl solution and dried over $\text{Na}_2\text{SO}_4$. Rotary evaporation followed by vacuum distillation (150–170° (0.4 mm)) gave 19.0 g (45% yield) of colorless **6**. Recrystallization from petroleum ether produced long white needles; mp 49.5–50.5° (lit. mp 52°); nmr $\tau$ 2.1 (m, 2, Ar*H*), 2.7 (m, 8, Ar*H*), 5.4 (q, 1, $J$ = 6.9 Hz, C*H*CH$_3$), 8.5 ppm (d, 3, $J$ = 6.9 Hz, CHC*H*$_3$).

**1,2-Diphenylpropanone Hydrazone.** A modification of the reported[30] method for preparing hydrazones was used in this synthesis. In a typical reaction 21 g of ketone (**6**; 0.1 mol) dissolved in 100 ml of absolute ethanol was added dropwise to a refluxing solution of 16 g (0.5 mol) of anhydrous hydrazine in 150 ml of absolute ethanol. The solution was refluxed for 20 hr after which half the solvent was removed by simple distillation. The solution was cooled in ice to induce crystallization; the resulting white solid was collected and dissolved in a minimum amount (*ca.* 1 l.) of petroleum ether. The solution afforded 13.3 g of fine, white needles, mp 83–85°. An additional 1.0 g was recovered from the mother liquor: yield, 14.3 g (64%); nmr $\tau$ 2.9 (m, 10, Ar*H*), 5.1 (s, 2 N*H*$_2$), 6.2 (q, 1, $J$ = 7.2 Hz, C*H*CH$_3$), 8.5 ppm (d, 3, $J$ = 7.2 Hz, CHC*H*$_3$). The hydrazone was quite stable; it was tightly sealed and refrigerated until needed. *Anal.* Calcd for $\text{C}_{15}\text{H}_{16}\text{N}_2$: C, 80.32; H, 7.19; N, 12.49. Found:[40] C, 80.44; H, 6.93; N, 12.57.

**1,2-Diphenyldiazopropane (1).** A modification of the procedures of Smith and Howard, and Miller[30] was used to oxidize the hydrazone to the corresponding diazoalkane. All equipment coming in contact with the diazo solution was base washed (concentrated ammonia solution) and oven dried. The general method was to place 0.25 g (1.1 mmol) of 1,2-diphenylpropanone hydrazone, 0.35 g (2.9 mmol) of anhydrous magnesium sulfate, and 5.0 g (23 mmol) of yellow mercury(II) oxide in a 100-ml three-necked flask equipped with a magnetic stirrer, gas inlet, 50-ml addition funnel, and condenser with gas bubble counter. Dry nitrogen was slowly passed through the flask, and 50 ml of absolute ether was added. A freshly made saturated solution of potassium hydroxide in absolute ethanol (5–10 drops) was added to initiate the oxidation, and the flask was protected from light (aluminum foil) and cooled with an ice bath. A nitrogen atmosphere was maintained during the oxidation, which was accompanied by rapid darkening of the mercury(II) oxide and the formation of a pink solution. Two or three hour reaction times were used; 2 hr was found to be sufficient, and this minimized decomposition of **1** during the reaction. The solution was quickly suction filtered through a medium porosity glass fritted funnel, and the solvent was removed by a slow stream of dry nitrogen. The residual deep red oil (0.24 g, >96% yield by nmr) was identified as 1,2-diphenyldiazopropane (**1**) by its infrared (4.92 $\mu$, C=N=N),[19] its nmr [$\tau$ 3.0 (m, 10, Ar*H*), 6.1 (q, 1, $J$ = 7.0 Hz, C*H*CH$_3$), 8.4 ppm (d, 3, $J$ = 7.0 Hz, CHC*H*$_3$)], its absorption spectrum ($\lambda_{\text{max}}^{\text{hexane}}$ 516 nm ($\epsilon$ 36 ± 1); $\lambda_{\text{max}}^{\text{hexane}}$ 286 nm ($\epsilon$ $2.0 \times 10^4$)) and by the products of its decomposition (*vide infra*). The diazoalkane could not be crystallized, and its purity was measured by nmr spectroscopy; if an observable amount of hydrazone or other material was visible in the nmr spectrum the sample was discarded (about 4% impurity would have been observable by nmr). The neat diazo compound was unstable to light, heat, and air. In solution (absolute ether, hexane, or benzene) it could be refrigerated under nitrogen for *ca.* 1 week without significant decomposition, but this practice was not generally followed; rather the solution was consumed as quickly as possible. For thermal and photochemical decompositions a $1.0\text{–}3.0 \times 10^{-2}$ *M* benzene solution of **1** was generally used.

The general method for preparing 1,2-diphenyldiazopropane (**1**) described above was occasionally run on a larger scale (0.5–1.0 g of hydrazone), and in these cases the quantities of reagents were proportional.

**1,2-Diphenylpropanone Azine (7).** The general azine synthesis of Overberger and Gainer[24] was used. 1,2-Diphenylpropanone hydrazone (1.0 g, 4.5 mmol) and 0.94 g (4.5 mmol) of 1,2-diphenylpropanone (**6**) were dissolved in 15 ml of xylene and a few crystals of *p*-toluenesulfonic acid were added. The solution was placed in a flask equipped with a Dean–Stark trap filled with solvent, condenser, magnetic stirrer, and heating mantle; the solution was refluxed for 7 hr. The bright-yellow solution was cooled, washed twice with 0.1 *M* NaOH solution (30 ml) and twice with water (30 ml), and dried (saturated sodium chloride solution and magnesium sulfate). The solvent was removed (rotary evaporation), and a viscous yellow oil remained. Attempted recrystallizations of the oil from methanol were not successful, but petroleum ether did afford one crop of yellow "amorphous" solid: mp 93°; nmr $\tau$ 3.0 (m, 20, Ar*H*), 4.9 (m, 1, C*H*CH$_3$), 6.2 (m, 1, C*H*CH$_3$), 8.5 ppm (m, 6, CHC*H*$_3$). The upfield multiplets appeared to be at least

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[39] We wish to thank the National Science Foundation for a grant to Yeshiva University to help purchase this instrument.

[40] Analysis by Galbraith Laboratories, Inc., Knoxville, Tenn.

three sets of overlapping doublets ($J$ = 7.1 Hz), and those downfield appeared to be quartets ($J$ = 7.1 Hz); four distinct quartets were evident. The mother liquor did not yield more solid; the oil was chromatographed on alumina with the following sequence of solvents: pentane, pentane–benzene (50:50), benzene–ether (50:50), and ether. The fractions yielding a yellow oil having similar infrared spectra were combined; the nmr was similar to that of the solid.

**_p_-Chlorobenzene-_d_.** Magnesium turnings (5.0 g, 0.21 g-atom) were placed in a 250-ml three-necked flask equipped with a condenser and drying tube, addition funnel (125 ml), gas inlet, and magnetic stirrer. The flask was heated gently to remove moisture and allowed to cool, after which absolute ether (25 ml) was added. To initiate the reaction 10 ml of a solution of *p*-bromochlorobenzene (38.4 g, 0.2 mol in 120 ml of ether) was added. Dropwise addition of the dihalide was continued, and refluxing was controlled with the aid of an ice bath. When refluxing ceased the mixture was heated for 10 min; the solution was quenched by the dropwise addition of $D_2O$ (9.0 ml) and finally a solution of $D_2SO_4$ and DCl (previously prepared from 1.5 ml of sulfuryl chloride and 10 ml of $D_2O$). The mixture was stirred for 1 hr, washed with 5% HCl (200 ml), and extracted with ether. In addition to the usual treatment the ether layer was washed with 1 *M* KOH and 5% $Na_2CO_3$ solutions. The volume was reduced to *ca.* 100 ml by simple distillation, and the remaining liquid was distilled through a 6-in. Helipak column. A reflux ratio of 5:1 was used to collect the material boiling at 130–131°; yield, 16.8 g (74% of theory). Mass spectroscopy indicated 93.2% monodeuterated material.

**1-(_p_-Phenyl-_d_)-2-phenyl-1-propanol.** Magnesium turnings (3.95 g, 0.16 g-atom) were placed in a 250-ml three-necked flask equipped with a condenser and drying tube, gas inlet, addition funnel, and magnetic stirrer. The equipment was heated to remove water traces and allowed to cool. The reaction was initiated with a few drops of ethyl iodide and then the *p*-chlorobenzene-*d* (16.8 g, 0.15 mol) in 10 ml of tetrahydrofuran was slowly added so that refluxing was maintained and finally the mixture was refluxed for 2 hr after the addition was complete. 2-Phenylpropionaldehyde (25 g, 0.19 mol) in 40 ml of THF was added dropwise to the cooled Grignard reagent, after which refluxing was continued for 1 hr. The reaction mixture was stirred at room temperature overnight, and then slowly poured over a mixture of dilute sulfuric acid and ice. The organic layer was separated from the acid solution, which was extracted twice with ether. The combined organic solution was washed with water and dried (magnesium sulfate). Solvents were removed by distillation, and the residual liquid was vacuum distilled (Vigreux column). Several fractions were collected, and infrared, vlpc, and nmr analyses indicated which ones contained the desired product (*i.e.*, those collected at 130–140° (2.0 mm)); yield 16.7 g, 52% based upon *p*-chlorobenzene-*d*.

**1-(_p_-Phenyl-_d_)-2-phenylpropanone.** To 13.7 g (65 mmol) of 1-(*p*-phenyl-*d*)-2-phenyl-1-propanol and 26 g (89 mmol) of potassium dichromate dissolved in 60 ml of water was added dropwise 40 ml of concentrated sulfuric acid. The reaction became very dark, and the temperature was maintained below 70° by external cooling. When the acid addition was completed the solution was heated at 70° for 1 hr and cooled with an ice bath and by the addition of ice. The organic material was extracted twice with 50 ml of ether. The combined ethereal solution was washed with water and sodium bicarbonate solution until slightly basic, and then dried. The ether was removed (rotary evaporation), and the residual oil was vacuum distilled (Vigreux column). The fraction boiling at 110–115° (0.10 mm) was collected (7.5 g, 55%). This material was recrystallized from petroleum ether (mp 44–45°): nmr $\tau$ 2.1–3.1 (m, 9.2, Ar$H$), 5.5 (q, 1.0, $J$ = 6.6 Hz, C$H$CH$_3$), 2.6 ppm (d, 2.9, $J$ = 6.6 Hz, CHC$H_3$). Mass spectroscopy indicated 93.6% $d_1$ ketone.

**1-(_p_-Phenyl-_d_)-2-phenylpropanone Hydrazone.** The same procedure was used as in the preparation of the undeuterated hydrazone (*vide supra*): yield 1.17 g (64%) of colorless needles from petroleum ether; mp 82–83°; nmr $\tau$ 3.0 (m, 10, Ar$H$), 5.1 (s, 1.9, N$H_2$), 6.2 (q, 1.0, $J$ = 7.1 Hz, C$H$CH$_3$), 8.6 ppm (d, 3.2, $J$ = 7.1 Hz, CHC$H_3$).

**1-(_p_-Phenyl-_d_)-2-phenyldiazopropane (9).** The material was synthesized as above from 250 mg of deuterated hydrazone. No impurities were evident by nmr: ir 4.92 $\mu$[19] (strong); nmr $\tau$ 2.9 (m, 9.4, Ar$H$), 6.1 (q, 1, $J$ = 7.1 Hz, C$H$CH$_3$), 8.5 ppm (d, 3, $J$ = 7.1 Hz, CHC$H_3$). A fresh batch of **9** was used for the thermal and the photochemical decomposition.

**2,2-Diphenylpropionaldehyde.** The procedure of Tiffeneau and Dorlencourt[28] was used in the synthesis of 1,2-dihydroxy-1,2-diphenylpropane; this, in turn, was rearranged to the desired aldehyde by the method of Lévy.[29]

A solution of methylmagnesium iodide in anhydrous ether was prepared from methyl iodide (28.4 g, 0.20 mol) and magnesium turnings (4.6 g, 0.19 g-atom). Powdered benzoin (20.0 g, 0.095 mol) was added to the solution in small portions (*ca.* 2 g) with vigorous stirring. Additional ether was used to replace that lost by evaporation, and the mixture was refluxed 15 min. The reaction was quenched with ice and dilute hydrochloric acid. The aqueous layer was separated from the ether and extracted twice with ether. The combined organic layer was washed with dilute hydrochloric acid, and then with distilled water until neutral. The ether solution was dried, and the solvent was removed on a steam bath. The crude 1,2-dihydroxy-1,2-diphenylpropane solidified upon cooling: nmr $\tau$ 2.9 (m, 11, Ar$H$), 5.3 (s, 1, C$H$OH), 7.2 (s, 2, OH), 8.4 ppm (s, 3, CC$H_3$).

The glycol was refluxed 5 hr with 200 ml of an oxalic acid solution (150 g of $H_2C_2O_4 \cdot 2H_2O$). An infrared spectrum of the crude rearranged product indicated the presence of an aldehyde (1720 (C=O), 2720, 2820 cm$^{-1}$ (CHO)). The organic layer was separated from the aqueous solution, which was extracted twice with ether. The combined organic layer was washed twice with water (200 ml) and dried with saturated sodium chloride solution. The volume was reduced to 50 ml (steam bath) and further dried with magnesium sulfate. The remaining ether was removed under aspirator pressure, and the residual oil was distilled (bp 102–108° (0.1 mm)). Infrared and nmr spectroscopy were used to determine the purity of each fraction that was collected, and those which contained mainly the desired aldehyde were combined: ir 1720 (C=O), 2720 and 2820 cm$^{-1}$ (CHO); nmr $\tau$ 0.2 (s, 1, C$H$O), 2.9 (m, 12, Ar$H$), 8.3 ppm (s, 3, C$H_3$); yield 14 g, 70% of theory based upon benzoin.

**2,2-Diphenylpropionaldehyde Hydrazone.** To a refluxing solution of anhydrous hydrazine (16 g, 0.5 mol) in 150 ml of absolute ethanol was added dropwise 14 g (0.067 mol) of distilled 2,2-diphenylpropionaldehyde in 50 ml of ethanol. The solution was refluxed 20 hr, and half of the solvent was distilled. Cooling the solution did not induce precipitation of product, so it was washed twice with water (100 ml each) to separate the oily product from the hydrazine and ethanol. The aqueous layer was extracted twice with ether (50 ml each), and the organic material was combined with the oil. The resulting ethereal solution was washed with water until it was no longer basic to indicator paper. It was dried with saturated sodium chloride solution, and finally, with anhydrous magnesium sulfate. The volume was reduced to 50 ml (steam bath), and pentane was added until a cloudy solution was obtained. Cooling the solution induced separation of an oil which could not be crystallized. The solvent was removed (steam bath), and the nmr spectrum of the residual yellow oil was recorded: nmr $\tau$ 2.8 (s, 1, $H$C=N$_2$), 2.9 (m, 13, Ar$H$), 5.1 (s, 2.5, N$H_2$), 8.2 ppm (s, 3, C$H_3$). Impurities were evident at $\tau$ 8.5–8.7, so the aromatic integration was high. The neat oil became more intensely yellow upon standing (possibly because of azine formation), so it was dissolved in 100 ml of anhydrous ether and refrigerated. This crude solution of hydrazone was used to prepare 2,2-diphenyldiazopropane (**10**).

**2,2-Diphenyldiazopropane (10).** To 10 ml of the ethereal solution of 2,2-diphenylpropionaldehyde hydrazone (*ca.* 1 g, 4.5 mmol) was added 10.0 g (46 mmol) of yellow mercury(II) oxide, 1.0 g of anhydrous magnesium sulfate, and 5 drops of a freshly saturated solution of KOH in absolute ethanol. The mixture was protected from the light, cooled with an ice bath, and vigorously stirred. The mercury gradually darkened, and the solution changed from yellow to orange. After 4 hr the solid was filtered from the solution (medium porosity fritted funnel), and the solvent was removed by a stream of dry nitrogen. The residual orange oil bubbled profusely, so aliquots were removed for spectroscopic analyses and the bulk sample was dissolved in 25 ml of dry benezene and refrigerated. The nmr spectrum displayed numerous absorptions at $\tau$ 7.6–8.7 ppm in addition to the aromatic resonances ($\tau$ 3.0 ppm). Two were identified as methyl doublets of olefins **4** and **5**, but the vinyl protons were partly obscured by the aromatic resonance. A doublet identical with that of 1,1-diphenylpropene (**8**) was also present, and part of the vinyl quartet was evident: ir 2050 and 2000 cm$^{-1}$ (C=N=N);[19] vis $\lambda_{\max}^{\text{benzene}}$ *ca.* 510 nm. The crude sample was used in thermal and photochemical decomposition studies (*vide infra*) since neither the hydrazone nor the diazo compound (**10**) could be purified.

**Isolation and Identification of Products from the Decomposition of 1,2-Diphenyldiazopropane (1).** Several thermal decomposition samples of **1** (in benzene or toluene) were combined, and the solvents were removed by a slow stream of nitrogen. The residual yellow oil was dissolved in carbon tetrachloride, and its nmr spectrum was recorded. The crude mixture displayed peaks that were superimposable with those of authentic (*Z*)-1,2-diphenylpropene (**4**), (*E*)-1,2-diphenylpropene (**5**), 1,1-diphenylpropene (**8**), 1,2-diphenylpropanone (**6**), and the azines (**7**). Vlpc collection of the products (column G at 160°) was accomplished with separation of the mixture into two peaks. The first was identified as a mixture of **4** and **8** by comparison of the nmr spectra of collected material with those of the independently synthesized standards. Similarly, the second peak was identified as *E* olefin **5** and ketone **6**. The azines did not elute.

Further evidence of the identity of the products, in addition to nmr and vlpc comparisons, was provided by the decomposition of 1-(*p*-phenyl-*d*)-2-phenyldiazopropane (**9**). Ozonolysis of the vlpc collected products (column E at 160° or column D at 175°) furnished material identified as acetophenone, benzaldehyde, and benzophenone, compounds expected from ozonolysis of olefins **4**, **5**, and **8**.

**Determination of Olefin Yields in the Thermal Decomposition of 1 at 75°.** A solution of 115 mg (0.52 mmol) of 1,2-diphenyldiazopropane (**1**) dissolved in 17 ml of benzene was placed in a clean Pyrex tube (15 mm × 255 mm) and sealed under water aspirator pressure. The tube was immersed in a bath at 75.0 ± 0.2° for 140 hr, after which it was cooled and opened. Nmr analysis in Silanor C (after removal of the benzene) using 4.7 mg ($1.75 \times 10^{-2}$ mmol) of Micheler's ketone [4,4'-bis(dimethylamino)benzophenone] as a standard showed that 38 mg of (*Z*)- and (*E*)-1,2-diphenylpropene, 15 mg of 1,1-diphenylpropene, and 30 mg of 1,2-diphenylpropanone were present; the total yield of olefins was 50%. The remainder was ketone (30%) and azine (20%).

**Thermal Decomposition Reactions of 1,2-Diphenyldiazopropane (1).** Two general decomposition methods, refluxing solutions or sealed tube reactions, were used. All equipment (except disposable pipets) coming in contact with the diazo solution was cleaned, base washed (concentrated aqueous ammonia solution), and oven dried prior to use.

The azine, ketone (**6**), and olefins (**4**, **5**, and **8**) were stable under the thermal decomposition reaction conditions. No significant change in composition occurred after a mixture of these materials was heated in benzene (sealed tube) for 24 hr at 150° (normal decomposition reactions of **1** at this temperature required only 10 min). That olefins **4** and **5** did not equilibrate in these reactions is indicated by the observation that the **4**:**5** ratio after 24 hr at 150° (0.59) was the same as that before heating (0.60); these values are far from the reported[41] thermodynamic equilibrium ratios (**4**:**5** = 0.274 at 139°, 0.286 at 200°).

**Procedure A.** To 10 ml of dry refluxing solvent (benzene, toluene, *o*-xylene, or mesitylene) contained in a 25-ml round-bottomed flask equipped with a thermometer, condenser and gas bubble counter, magnetic stirrer, and addition funnel with a gas inlet tube, was added 15 ml of a $1.1 \times 10^{-2}$ *M* solution of **1**. The addition was slow enough that refluxing did not cease, and a dry nitrogen atmosphere was maintained throughout the addition and decomposition. The flask was protected from light and refluxing was continued until the bright red color changed to yellow, or until the 4.9-$\mu$ band in the infrared spectrum of aliquots disappeared. The reaction mixture was vlpc analyzed (column A or B at 150°), and the relative peak areas were measured. The results of these experiments are summarized in Tables VII–X which show the relative area percentages of products from the decomposition of **1**.

**Table VII.** Products from Decomposition of **1** in Refluxing Benzene at 80° (Rel %)

| No. | **8** | **6** | **4** | **5** | **4**:**5** | (**4** + **5**):**8** |
|---|---|---|---|---|---|---|
| 1 | 15 | 11 | 35 | 40 | 0.88 | 5.0 |
| 2 | 10 | 11 | 33 | 44 | 0.75 | 7.7 |
| 3 | 12 | 5.7 | 38 | 38 | 1.00 | 6.3 |
| 4 | 9.3 | 1.8 | 40 | 47 | 0.85 | 9.4 |
| | | | | | Av 0.87 | 7.1 |

**Table VIII.** Products from Decomposition of **1** in Refluxing Toluene at 110° (Rel %)

| No. | **8** | **6** | **4** | **5** | **4**:**5** | (**4** + **5**):**8** |
|---|---|---|---|---|---|---|
| 1 | 13 | 14 | 30 | 43 | 0.70 | 5.6 |
| 2 | 16 | 12 | 25 | 46 | 0.54 | 4.4 |
| 3 | 15 | 3.7 | 32 | 48 | 0.67 | 5.3 |
| 4 | 17 | 5.6 | 31 | 41 | 0.76 | 4.2 |
| | | | | | Av 0.67 | 4.9 |

**Table IX.** Products from Decomposition of **1** in Refluxing Xylene at 144° (Rel %)

| No. | **8** | **6** | **4** | **5** | **4**:**5** | (**4** + **5**):**8** |
|---|---|---|---|---|---|---|
| 1 | 14 | 4.0 | 31 | 51 | 0.61 | 5.8 |
| 2 | 13 | 2.5 | 33 | 51 | 0.65 | 6.5 |
| 3 | 10 | 2.8 | 33 | 47 | 0.70 | 8.0 |
| 4 | 7.6 | 1.6 | 39 | 50 | 0.78 | 11.7 |
| | | | | | Av 0.68 | 8.0 |

**Table X.** Products from Decomposition of **1** in Refluxing Mesitylene at 165° (Rel %)

| No. | **8** | **6** | **4** | **5** | **4**:**5** | (**4** + **5**):**8** |
|---|---|---|---|---|---|---|
| 1 | 9.8 | 2.0 | 36 | 51 | 0.70 | 8.9 |
| 2 | 11 | 2.0 | 33 | 51 | 0.65 | 7.6 |
| 3 | 13 | 2.8 | 30 | 49 | 0.61 | 6.1 |
| 4 | 12 | 3.3 | 31 | 52 | 0.60 | 6.9 |
| 5 | 13 | 1.8 | 30 | 51 | 0.59 | 6.2 |
| 6 | 11 | 2.2 | 33 | 52 | 0.63 | 7.7 |
| 7 | 11 | 2.0 | 34 | 51 | 0.66 | 7.7 |
| 8 | 12 | 1.8 | 32 | 52 | 0.62 | 7.0 |
| | | | | | Av 0.63 | 7.3 |

In this and succeeding tables, only the compound numbers used in the text will be employed. They are, once again, as follows: 1,1-diphenylpropene, **8**; 1,2-diphenylpropanone, **6**; (*Z*)-1,2-diphenylpropene, **4**; (*E*)-1,2-diphenylpropene, **5**.

**Procedure B.** Pyrex tubes (cleaned, base washed, and oven dried; 8 mm o.d. × 150 mm) containing 0.5–1.0 ml of $1.1 \times 10^{-2}$ *M* solution of **1** in benzene were degassed 5–15 min with dry nitrogen, cooled in Dry Ice, and sealed under vacuum (15 mm from an aspirator). The tubes were warmed to room temperature, protected from light, and then completely immersed in an oil bath thermostated at the desired temperature. (Maximum deviation from the set temperature was ±0.3°. Immersion generally caused the temperature of the bath to fall a maximum of 2°, but recovery to the set temperature occurred in less than 1 min.) Decompositions were run until the red color of **1** was replaced by the bright yellow of the azines, after which the tubes were cooled, opened, and vlpc analyzed (column A, B, or C) at 150°. The results of these experiments are summarized in Tables XI–XIV, which show the relative area percentages of products from decomposition of **1**.

**Table XI.** Products from Decomposition of **1** in Benzene at 75° (Rel %)

| No. | **8** | **6** | **4** | **5** | **4**:**5** | (**4** + **5**):**8** |
|---|---|---|---|---|---|---|
| 1 | 17 | 14 | 31 | 37 | 0.84 | 4.0 |
| 2 | 16 | 16 | 30 | 38 | 0.79 | 4.2 |
| 3 | 16 | 14 | 33 | 35 | 0.94 | 4.2 |
| 4 | 15 | 18 | 26 | 37 | 0.70 | 4.2 |
| 5 | 20 | 19 | 19 | 36 | 0.53 | 2.8 |
| 6 | 19 | 19 | 21 | 36 | 0.58 | 3.0 |
| | | | | | Av 0.73 | 3.7 |

**Photochemical Decompositions of 1,2-Diphenyldiazopropane (1). Lamps and Filters.** The following light sources were used: (a) a General Electric 100-W medium-pressure mercury lamp, Model H100-A4/T; (b) a General Electric 400-W medium-pressure mercury lamp, Model H400A33-1. The filters used are as follows.

**Filter solution A** was composed of copper(II) chloride dihydrate (20 g, 1.2 mol) and anhydrous calcium chloride (27 g, 0.24 mol)

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[41] A. Zwierzak and H. Pines, *J. Org. Chem.*, **27**, 4084 (1962); D. J. Cram, F. D. Greene, and C. H. DePuy, *J. Amer. Chem. Soc.*, **78**, 790 (1956).

**Table XII.** Products from Decomposition of **1** in Benzene at 100° (Rel %)

| No. | 8 | 6 | 4 | 5 | 4:5 | (4 + 5):8 |
|---|---|---|---|---|---|---|
| 1 | 18 | 6.5 | 29 | 45 | 0.64 | 4.1 |
| 2 | 14 | 7.1 | 32 | 45 | 0.71 | 5.5 |
| 3 | 16 | 7.3 | 32 | 44 | 0.73 | 4.8 |
| 4 | 16 | 21 | 19 | 39 | 0.49 | 3.6 |
| 5 | 17 | 18 | 19 | 40 | 0.48 | 3.5 |
| 6 | 17 | 14 | 20 | 42 | 0.48 | 3.6 |
| 7 | 18 | 15 | 22 | 41 | 0.54 | 3.5 |
| 8 | 19 | 15 | 22 | 40 | 0.55 | 3.3 |
| 9 | 18 | 14 | 23 | 40 | 0.58 | 3.5 |
| 10 | 18 | 14 | 23 | 40 | 0.58 | 3.5 |
|  |  |  |  |  | Av 0.58 | 3.9 |

**Table XIII.** Products from Decomposition of **1** in Benzene at 125° (Rel %)

| No. | 8 | 6 | 4 | 5 | 4:5 | (4 + 5):8 |
|---|---|---|---|---|---|---|
| 1 | 15 | 4.6 | 30 | 48 | 0.62 | 5.2 |
| 2 | 15 | 4.8 | 30 | 48 | 0.62 | 5.2 |
| 3 | 15 | 4.9 | 30 | 48 | 0.62 | 5.2 |
| 4 | 19 | 3.6 | 24 | 48 | 0.50 | 3.8 |
| 5 | 19 | 3.2 | 24 | 49 | 0.49 | 3.8 |
| 6 | 19 | 3.5 | 23 | 48 | 0.48 | 3.7 |
| 7 | 20 | 5.2 | 23 | 48 | 0.48 | 3.6 |
| 8 | 18 | 12 | 22 | 44 | 0.50 | 3.7 |
| 9 | 19 | 13 | 20 | 44 | 0.45 | 3.4 |
| 10 | 18 | 12 | 24 | 43 | 0.56 | 3.7 |
| 11 | 19 | 12 | 20 | 43 | 0.46 | 3.3 |
|  |  |  |  |  | Av 0.52 | 4.0 |

**Table XIV.** Products from Decomposition of **1** in Benzene at 150° (Rel %)

| No. | 8 | 6 | 4 | 5 | 4:5 | (4 + 5):8 |
|---|---|---|---|---|---|---|
| 1 | 15 | 8.0 | 29 | 47 | 0.62 | 5.1 |
| 2 | 16 | 8.2 | 27 | 47 | 0.57 | 4.6 |
| 3 | 16 | 8.9 | 27 | 46 | 0.59 | 4.6 |
| 4 | 16 | 2.2 | 29 | 51 | 0.57 | 5.0 |
| 5 | 17 | 2.5 | 27 | 49 | 0.55 | 4.5 |
| 6 | 12 | 2.5 | 32 | 50 | 0.64 | 6.8 |
| 7 | 20 | 2.1 | 23 | 51 | 0.45 | 3.7 |
| 8 | 19 | 2.2 | 23 | 50 | 0.46 | 3.8 |
| 9 | 20 | 2.6 | 22 | 50 | 0.44 | 3.6 |
| 10 | 15 | 5.3 | 28 | 48 | 0.58 | 5.1 |
| 11 | 14 | 12 | 26 | 45 | 0.58 | 5.1 |
| 12 | 12 | 12 | 30 | 45 | 0.66 | 6.2 |
| 13 | 14 | 16 | 24 | 43 | 0.56 | 4.8 |
| 14 | 15 | 16 | 22 | 43 | 0.51 | 4.3 |
| 15 | 15 | 16 | 24 | 43 | 0.56 | 4.5 |
|  |  |  |  |  | Av 0.56 | 4.8 |

dissolved in 100 ml of water; the solution was made slightly acidic by hydrochloric acid addition. A 1.0-cm path length of this solution had an absorbance <2.0 between 480 and 610 nm, and a maximum transmittance at 533 nm. This solution is part of one described by Calvert and Pitts.[25] The filter was shown not to isomerize the 1,2-diphenylpropenes (**4** and **5**) or to decompose 1,1-diphenylpropene (**8**), 1,2-diphenylpropanone (**6**), or its azine (**7**).

**Filter solution B** was composed of copper(II) sulfate pentahydrate (60 g, 0.24 mol), sodium nitrite (75 g, 1.1 mol), and 80 ml of concentrated ammonia solution. A 1.0-cm path had an absorbance <2.0 between 400 and 482 nm, and a maximum transmittance at 420 nm. This also was described by Calvert and Pitts.[25] This filter did not isomerize olefins **4** and **5**, nor did it decompose the compounds **6**, **7**, or **8**.

**Filter no. PC-1**, manufactured by Coleman Instrument Corp., was also used. It had an absorbance >2.0 at wavelengths shorter than 400 nm. Olefins **4** and **5** were photostable to light transmitted by this filter.

**Photolysis Methods.** Some photolyses were conducted on 100 ml of a $10^{-3}$ *M* solution of **1** in benzene using filter solution B circulated through the jacket of a 100-W lamp and cooled by heat exchange. The temperature was maintained at *ca.* 17°. The solution was degassed throughout the irradiation, which was continued until the pink color of the diazo compound faded. The samples were then vlpc analyzed (column A at 150°).

More often photolyses were run in Pyrex tubes (8 mm × 150 mm) that contained *ca.* 1 ml of $1.1 \times 10^{-2}$ *M* solution of **1** in benzene. The solutions were degassed 30 min with dry nitrogen, sealed with a septum, and suspended in a water bath maintained at 20°. Irradiations were conducted with a 400-W lamp cooled with tap water and surrounded by an insert containing the filter solution. Analysis was by vlpc (column B or C at 150°).

A third photolysis method was to place the degassed solution of **1** in a 1-cm cuvette, and to place it in tandem with a glass filter or with a 1-cm cuvette containing filter solution. Light from a 400-W lamp was passed through the filter and then to the solution. The cuvettes were cooled with a stream of water. The reaction was monitored by measuring the intensity of the 516-nm absorption band of the diazo compound, and analyzed by vlpc (column B or C at 150°).

The results of photolyses are listed in Table XV.

**Table XV.** Products from Photochemical Decomposition of **1** in Benzene (Rel %)

| No. | 8 | 6 | 4 | 5 | 4:5 | (4 + 5):8 |
|---|---|---|---|---|---|---|
|  |  |  | Filter A |  |  |  |
| 1 | 16 | 39 | 19 | 18 | 1.0 | 2.3 |
| 2[a] | 19 | 38 | 19 | 19 | 1.0 | 2.0 |
| 3 | 26 | 26 | 19 | 27 | 0.70 | 1.8 |
| 4 | 30 | 10 | 27 | 33 | 0.82 | 2.0 |
| 5 | 33 | 5.1 | 25 | 37 | 0.68 | 1.9 |
| 6 | 33 | 5.7 | 25 | 36 | 0.69 | 1.8 |
| 7 | 32 | 14 | 22 | 32 | 0.69 | 1.7 |
| 8 | 32 | 14 | 22 | 33 | 0.67 | 1.7 |
|  |  |  |  |  | Av 0.78 | 1.9 |
|  |  |  | Filter B |  |  |  |
| 9 | 29 | 8.1 | 29 | 34 | 0.85 | 2.2 |
| 10 | 27 | 12 | 28 | 33 | 0.85 | 2.3 |
| 11 | 33 | 3.8 | 29 | 35 | 0.83 | 1.9 |
| 12 | 32 | 4.9 | 28 | 35 | 0.80 | 2.0 |
| 13 | 32 | 5.8 | 28 | 34 | 0.82 | 1.9 |
| 14[a] | 23 | 33 | 20 | 24 | 0.83 | 1.9 |
| 15 | 32 | 11 | 26 | 31 | 0.84 | 1.8 |
| 16[a] | 23 | 32 | 20 | 25 | 0.80 | 2.0 |
|  |  |  |  |  | Av 0.83 | 2.0 |
|  |  |  | Filter No. PC-1 |  |  |  |
| 17 | 28 | 19 | 24 | 28 | 0.86 | 1.9 |

[a] To partial completion.

**Photosensitized Decomposition of 1,2-Diphenyldiazopropane (1).** The absorption spectra of **1** and the sensitizers, fluorenone and benzil, were integrated (cut and weigh method) in the region of transmittance of filter solution B. For a $2.3 \times 10^{-2}$ *M* solution of **1** in benzene 99% light absorption by fluorenone was accomplished with a 0.44 *M* solution and 96% light absorption by benzil with a 0.38 *M* solution. Aliquots (1 ml) of these solutions were placed in Pyrex tubes, degassed 30 min, and irradiated (filter solution B) to partial completion (<25% by visible spectroscopy). Samples were quenched with dimethyl acetylenedicarboxylate and vlpc analyzed (column B or C at 150°). Occasionally samples where chromatographed on alumina to remove the sensitizer and this did not change the **4**:**5** ratio. Table XVI summarizes the results. In two runs a solution of **1** in benzene was used as the filter together with filter B.

**Thermal Decomposition of 1-(*p*-Phenyl-*d*)-2-phenyldiazopropane (9).** A solution of **9** (0.25 g, 1.1 mmol) in 25 ml of benzene was equally divided among four medium-wall Pyrex tubes (13 mm × 250 mm). Each was degassed with nitrogen, cooled in Dry Ice, and sealed under aspirator pressure. The tubes were simultaneously heated for 13 hr in the dark at 100.0 ± 0.4°, cooled, and vlpc analyzed (column B at 150°). The results are indicated in Table XVII.

The volume of each solution was reduced to *ca.* 0.5 ml by a slow stream of nitrogen, and they were combined. The solution was further reduced to *ca.* 0.5 ml of a yellow oil which was eluted with hexane through an 11-cm column of alumina to remove the azine.

**Table XVI.** Products from the Photosensitized Decomposition of **1** in Benzene (Rel %)

| Concn **1**, $M \times 10^2$ | Sensitizer[a] | Concn sensitizer, $M \times 10$ | % light abs. by sensitizer | **8** | **6** | **4** | **5** | **4**:**5** | (**4** + **5**):**8** |
|---|---|---|---|---|---|---|---|---|---|
| 7.0[b] | F | 1.8 | *c* | 13 | 65 | 7.5 | 14 | 0.54 | 1.6 |
| 7.0 | F | 1.8 | *c* | 26 | 34 | 15 | 24 | 0.62 | 1.5 |
| 2.3 | F | 4.4 | 99 | 30 | 30 | 17 | 21 | 0.81 | 1.3 |
| 2.3 | F | 4.4 | 99 | 32 | 24 | 20 | 22 | 0.91 | 1.3 |
| 2.3 | F | 1.1 | 96 | 26 | 39 | 13 | 22 | 0.59 | 1.3 |
| 2.3 | F | 1.1 | 96 | 24 | 41 | 13 | 22 | 0.59 | 1.5 |
| | | | | | | | | Av 0.68 | 1.4 |
| 7.0[b] | B | 2.8 | *c* | 36 | 16 | 15 | 32 | 0.47 | 1.3 |
| 7.0 | B | 2.8 | *c* | 34 | 21 | 14 | 31 | 0.45 | 1.3 |
| 2.3 | B | 3.8 | 96 | 29 | 28 | 15 | 27 | 0.56 | 1.4 |
| 2.3 | B | 3.8 | 96 | 27 | 33 | 14 | 25 | 0.56 | 1.4 |
| | | | | | | | | Av 0.51 | 1.4 |

[a] F = fluorenone; B = benzil. [b] Light filtered by both **1** ($1.4 \times 10^{-2}$ *M*) and filter solution B. [c] Not measured.

**Table XVII.** Products from Thermal Decomposition of **9** in Benzene at 100° (Rel %)

| No. | **8** | **6** | **4** | **5** | **4**:**5** | (**4** + **5**):**8** |
|---|---|---|---|---|---|---|
| 1 | 6.4 | 12 | 38 | 43 | 0.88 | 13 |
| 2 | 9.9 | 12 | 36 | 41 | 0.88 | 7.8 |
| 3 | 10 | 13 | 35 | 42 | 0.83 | 7.7 |
| 4 | 8.4 | 13 | 38 | 41 | 0.93 | 9.4 |
| | Av 8.7 | 12.5 | 37 | 42 | 0.88 | 9.5 |

Fractions containing the olefinic products (as indicated by vlpc) were combined. The *Z*/*E* ratio (0.87) of the eluent was the same as those of the crude solutions. The olefins were vlpc collected (column D at 190°) and dissolved in methylene chloride. Yields: (*E*)-1,2-diphenylpropene (**5**), 20 mg; (*Z*)-1,2-diphenylpropene (**4**) contaminated with 1,1-diphenylpropene (**8**), 31 mg. Vlpc analysis (column B at 150°) of the collected *E* fraction showed 3.6% *Z* olefin and 1.2% 1,1-diphenylpropene. Vlpc analysis of the collected *Z* olefin showed 19.8% 1,1-diphenylpropene and 1.8% (*E*)-1,2-diphenylpropene.

The *E* fraction was ozonized and the benzaldehyde and acetophenone products were separated and collected by vlpc (column D at 135°). Mass spectral analysis of the acetophenone indicated less than 1% $d_1$ material.

The *Z* fraction (containing 1,1-diphenylpropene) was also ozonized and treated the same as the *E* product. Mass spectral analysis of the acetophenone indicated less than 1% acetophenone-$d_1$.

**Photochemical Decomposition of 1-(*p*-Phenyl-*d*)-2-phenyldiazopropane (9).** A solution of **9** (0.25 g, 1.1 mmol) in 25 ml of benzene was equally divided between two Pyrex tubes (16 mm × 210 mm). Each was degassed with nitrogen (30 min) and sealed with a septum. They were simultaneously irradiated with a 400-W Hg lamp (filter solution B) for 48 hr at 15°. Each sample was quenched with 100 μl of dimethyl acetylenedicarboxylate and vlpc analyzed (column B at 150°). The results are shown in Table XVIII.

**Table XVIII.** Products from Photolysis (Filter B) of **9** in Benzene (Rel %)

| No. | **8** | **6** | **4** | **5** | **4**:**5** | (**4** + **5**):**8** |
|---|---|---|---|---|---|---|
| 1 | 33 | 7.5 | 27 | 33 | 0.82 | 1.8 |
| 2 | 33 | 6.5 | 28 | 33 | 0.85 | 1.8 |

The volume of each tube was reduced to *ca.* 1 ml by a slow steam of nitrogen, and the samples were combined. The solution was further reduced in volume and chromatographed on an 11-cm column of neutral alumina (80–100 mesh, Brockman Activity 1) with hexane as eluent. Fractions which contained products were combined and reduced in volume to *ca.* 1 ml. (Chromatography did not change the *Z*/*E* ratio.) Vlpc collection of the olefins (column E at 160°) resulted in the following yields: (*E*)-1,2-diphenylpropene (**5**), 32 mg; (*Z*)-1,2-diphenylpropene (**4**) contaminated with 1,1-diphenylpropene (**8**), 62 mg. Vlpc analysis of the collected *E* fraction showed 1.9% *Z* and 2.7% of the 1,1 isomer. The *Z* fraction contained 1.6% of *E* olefin and 53.7% of 1,1-diphenylpropene.

Each olefin fraction was dissolved in methylene chloride-pyridine and ozonized. The benzaldehyde and acetophenone products were separated and collected by vlpc (column D at 135°). Mass spectral analysis of the acetophenone from the (*E*)-1,2-diphenylpropene indicated less than 0.5% $d_1$ material. The *Z* fraction (containing 1,1-diphenylpropene) was also ozonized; mass spectral analysis of the acetophenone showed less than 1% acetophenone-$d_1$.

**Ozonolysis of Olefin Mixtures.** The ozonolysis method of Conia and Leriverend[42] was followed. Methylene chloride–pyridine at −78° was the solvent used and the progress of the reaction was followed by thin-layer chromatography (silica gel, 2% methanol in pentane). After acid washing, the organic layer showed *ca.* 57% of benzaldehyde and *ca.* 43% of acetophenone by vlpc (column F at 160°). Purification was by vlpc.

**Thermal and Photochemical Decomposition of 2,2-Diphenyldiazopropane (10).** Since neither the hydrazone nor the diazo compound (**10**) could be adequately purified the reactions were run on a crude sample of **10**. Two tubes, each containing 1 ml of a $10^{-2}$ *M* solution of **10** in benzene, were degassed 30 min, cooled in Dry Ice, and sealed under aspirator pressure. They were shielded from light while being heated at 100 ± 10° for 3 hr, cooled, and analyzed by vlpc (column B at 150°). (Samples were yellow after 2 hr.) Several impurities were evident, but peaks having retention times identical with those of olefins **4** and **5** were integrated. These values are reported in Table XIX.

**Table XIX.** Products from Thermal and Photochemical Decomposition of 2,2-Diphenyldiazopropane (**10**) (Rel %)

| Sample | **8** | **4** | **5** | **4**:**5** |
|---|---|---|---|---|
| 1[a] | 16 | 34 | 51 | 0.67 |
| 2[a] | 15 | 33 | 52 | 0.63 |
| 3[b] | 16 | 31 | 53 | 0.58 |
| 4[b] | 16 | 30 | 54 | 0.56 |
| 5[c] | 20 | 33 | 47 | 0.70 |

[a] Heated at 100 ± 10° for 3 hr. [b] Photolyzed 24 hr (filter solution B) and quenched. [c] Sample at $t_0$ (partially decomposed while standing).

Two other tubes, each also containing 1 ml of the benzene solution of **10**, were degassed ($N_2$) and irradiated (filter solution B) at 20° for 24 hr. Samples were quenched by a drop of dimethyl acetylenedicarboxylate and analyzed by vlpc (column B at 150°). The photolysis did not go to completion, as indicated by the slightly orange color of the solution before quenching. Table XIX also lists the analysis of these samples.

Sample no. 2 was reduced in volume by a stream of nitrogen to *ca.* 0.25 ml. The yellow oil was dissolved in carbon tetrachloride

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(42) J. M. Conia and P. Leriverend, *C. R. Acad. Sci.*, **250**, 1078 (1960).

and its nmr and infrared spectra were recorded. Methyl absorptions ($\tau$ 7.8, 7.9, and 8.2 ppm) identical with those of (*E*)- and (*Z*)-1,2-diphenylpropene and 1,1-diphenylpropene, respectively, were prominent. The vinyl absorptions were partially obscured by the aromatic resonances. Several other materials were also evident in the $\tau$ 8.0-ppm region; judging from the yellow color of the solution it was presumed that azines were responsible for these absorptions.

**Quenching of 1,2-Diphenyldiazopropane (1) with Dimethyl Acetylenedicarboxylate.** Dimethyl acetylenedicarboxylate (DMADC) was found to be an efficient quencher of 1,2-diphenyldiazopropane (**1**); a solution of **1** was rapidly decolorized after the addition of the acetylene. Furthermore, analysis of a freshly prepared solution of **1** after quenching indicated only trace amounts of olefins relative to the 1,2-diphenylpropanone (**6**) present.

Table XX indicates that use of dimethyl acetylenedicarboxylate to quench **1** had no effect upon the products or the analyses. In each case the difference between the normal analysis and that of the quenched sample was small.

**Table XX.** Effect of Dimethyl Acetylenedicarboxylate upon Analyses of Products from Decomposition of **1** (Rel %)

| Sample[a] | 8 | 6 | 4 | 5 | 4:5 | (4 + 5):8 |
|---|---|---|---|---|---|---|
| 1N | 15 | 18 | 26 | 36 | 0.72 | 4.1 |
| 1Q | 15 | 18 | 26 | 37 | 0.70 | 4.2 |
| 2N | 19 | 15 | 22 | 40 | 0.55 | 3.3 |
| 2Q | 19 | 16 | 21 | 40 | 0.52 | 3.2 |

[a] Sample 1 was decomposed at 75° and sample 2 at 100°; N = normal analysis, Q = dimethyl acetylenedicarboxylate added prior to analysis.

Isolation and tentative identification of the addition product of DMADC and 1,2-diphenyldiazopropane were accomplished as follows. An ethereal solution (20 ml) of dimethyl acetylenedicarboxylate (90 mg, 0.60 mmol) was gradually added to 125 mg (0.56 mmol) of freshly prepared 1,2-diphenyldiazopropane (**1**) in 35 ml of ether. The resulting colorless solution was refluxed for 10 min, and the solvent was removed on a steam bath. The residual light yellow oil would not crystallize: nmr $\tau$ 2.9 (m, 14, Ar*H*), 4.8 (q, 1, $J$ = 7.0 Hz, C*H*CH$_3$), 6.3 (m, 15, CO$_2$C*H*$_3$), 8.2 ppm (d, 3, $J$ = 7.0 Hz, CHC*H*$_3$). Excess DMADC accounts for the extra ester methyls; the absorption at $\tau$ 6.3 appeared to be several singlets, ir 1720–1740 cm$^{-1}$ (C=O). The oil was vlpc collected (column E at 200°); the infrared spectrum of the collected material was nearly identical with that of the original compound. Mass spectral analysis of the vlpc collected material displayed an intense peak at *m/e* 364 in addition to an abundance of fragmentation ions (75 eV). At lower voltages (10–20 eV) the *m/e* 364 peak persisted, but fragmentation still occurred. Major ions at *m/e* 364, 349, 332, 317, 273, 260, 229, 172, and 105 (base peak).

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# Free-Radical Rearrangements in the Thermal Decomposition of *tert*-Butylperoxy 3-(1-Phenylcyclopropyl)propanoate, 4-(1-Phenylcyclopropyl)butanoate, and 5-(1-Phenylcyclopropyl)pentanoate

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**Abstract:** Decomposition of *tert*-butylperoxy 3-(1-phenylcyclopropyl)propanoate (**4**), 4-(1-phenylcyclopropyl)-butanoate (**14**), and 5-(1-phenylcyclopropyl)pentanoate (**29**) yields the corresponding alkyl radicals which are studied by esr; the barrier to rotation about C$_\beta$–C$_\gamma$ for the alkyl radicals produced from **4** and **14** gives a distinct inequivalency in the $\beta$ hydrogens. The yields of assigned products from thermal decomposition of **14** and **29** in benzene are greater than 84% and from **4**, greater than 93%. Products from both the cyclopropylethyl and the previously unobserved cyclopropylbutyl radical rearrangements have been detected, although in low yield. Ar$_{2-5}$, Ar$_{2-6}$, and Ar$_{2-7}$ radical rearrangement products are formed and their yields compared to give an estimate of relative reactivity in the formation of five-, six-, and seven-membered rings. No product from the cyclopropylcarbinyl radical rearrangement, expected in the process yielding Ar$_{2-n}$ rearrangement products, is observed; this result is discussed in terms of the requirements for the cyclopropylcarbinyl radical rearrangement. The identity and extent of hydrogen transfer reactions are also presented and discussed.

Highly strained cycloalkanes are well suited to studies of free-radical reactions at saturated carbon. In particular, substrates containing cyclopropane rings have been used extensively in studies of homoallylic rearrangements[3] and homolytic substitution reactions.[4]

The rearrangements of organic free radicals generally parallel but are less common than those of carbenium

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