The Thermal and the Photolytic Decomposition of 1-Phenyldiazoethane

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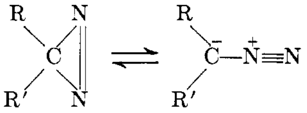
The thermal and the photolytic decomposition of 1-phenyldiazoethane is described and the mechanisms which may explain the formation of the observed products are discussed.

Our interest in cyclic azo compounds coupled with the fact that diazirines (I) and diazoalkanes (II) are valence tautomers[1] led us to investigate the chemistry of these compounds. Recently Schmitz and Ohme[2] reported that phenylmethyldiazirine (III) thermally decomposed to give styrene. This is to be contrasted with the behavior of 1-phenyldiazoethane (IV) which gave acetophenone azine as the sole product of decomposition. No styrene could be detected.[3]



I II

The purpose of this work was to investigate the causes of these unusual findings and to elucidate the mechanisms involved.

Results

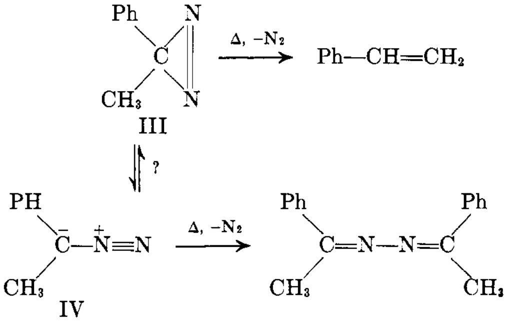
The thermal decomposition of 1-phenyldiazoethane was carried out by dropping a hexane solution of the diazoalkane into boiling benzene and by refluxing the red solution until complete decomposition had occurred. The decomposition product consisted essentially of acetophenone azine. Trace amounts of acetophenone and of benzoic acid were detected. Careful examination of the residue from the separation of the azine failed to reveal the presence of any styrene. Similarly, no trace of 2,3-diphenylbutane could be detected.

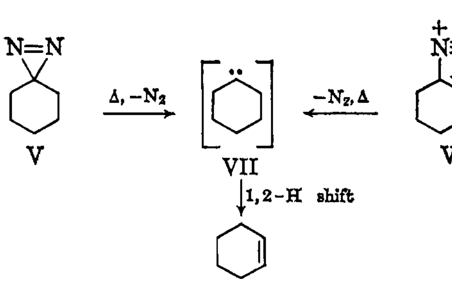
However, when a hexane solution of 1-phenyldiazoethane was photolyzed at 0–5° by a Hanovia high pressure mercury immersion lamp, three hydrocarbons were isolated by the careful work-up of the residue from the separation of acetophenone azine, the main product of the decomposition (95%). Two of these were characterized as styrene and *trans*-α,α'-dimethylstilbene. The third hydrocarbon was tentatively identified as 1,2-diphenyl-1-methylcyclopropane. Again, no 2,3-diphenylbutane could be detected on careful examination of the residue.

We could not duplicate the synthesis of phenylmethyldiazirine (III) as reported by Schmitz and Ohme.[2] A product having the physical properties of the diazirine (III) was obtained in very small yield. This colorless liquid (A) slowly took on a reddish coloration (B) upon standing in the presence of light. The infrared spectrum of the reddish material (B) had a strong absorption at 2042 cm.$^{-1}$ ($\overset{-}{C}$—$\overset{+}{N}$≡N), while the colorless liquid (A) was devoid of any peaks in this region.[4]

Discussion

The thermal decomposition of phenylmethyldiazirine (III) to give styrene compared with that of 1-phenyldiazoethane (IV) which gave acetophenone azine is to be contrasted with the results of the thermal decomposition of pentamethylenediazirine (V) and of diazocyclohexane (VI); cyclohexene was isolated in 97% yield from V[2] and 100% yield from VI.[5] Similarly, purely aliphatic diazoalkanes generally give good yields of hydrocarbons. The introduction of a phenyl group evidently had a significant effect on the course of the decomposition, since no hydrocarbon could be isolated from the thermal decomposition of 1-phenyldiazoethane. Presumably, the decomposition of V and VI must have had a common intermediate, the singlet state carbene (VII) which underwent a 1,2-hydrogen shift to give cyclohexene. The formation of a divalent carbon (phenylmethylcarbene) is not essential in the generation of acetophenone azine from 1-phenyldiazoethane. In fact, it is probably not at all involved since no product resulting from hydrogen abstraction (from solvent) by the triplet state species was detected. The formation of acetophenone azine can be viewed as resulting *via* the dimerization of the diazoalkane.[6]





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[1] C. G. Overberger and J.-P. Anselme, *Tetrahedron Letters*, 1405 (1963). We suggest that the term *electroisomers* is more appropriate for the special cases involving dipolar species.

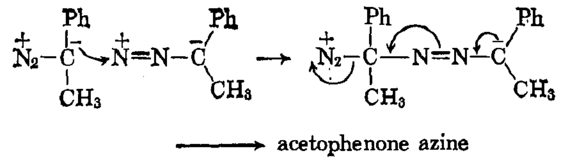
[2] E. Schmitz and R. Ohme, *Ber.*, **94**, 2166 (1961).

[3] H. Staudinger and A. Gaule, *ibid.*, **49**, 1887 (1916).

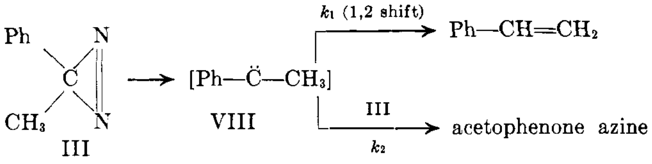
[4] See ref. 1 for a discussion of this phenomenon.

[5] L. Friedman and H. Schechter, *J. Am. Chem. Soc.*, **83**, 3159 (1963).

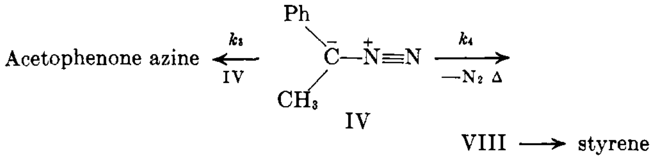
[6] P. Yates, D. G. Farnum, and D. H. Wiley, *Tetrahedron*, **18**, 881 (1962).



On the other hand, the formation of styrene from the thermal decomposition of phenylmethyldiazirine (III) must have involved the intermediacy of the corresponding carbene (VIII, singlet state). Schmitz[7] has noted the unusual inertness of diazirines (I) and it is reasonable to assume that a 1,2-hydrogen shift of the intermediate carbene would be favored over its reaction with unchanged diazirine ($k_1 >>> k_2$).

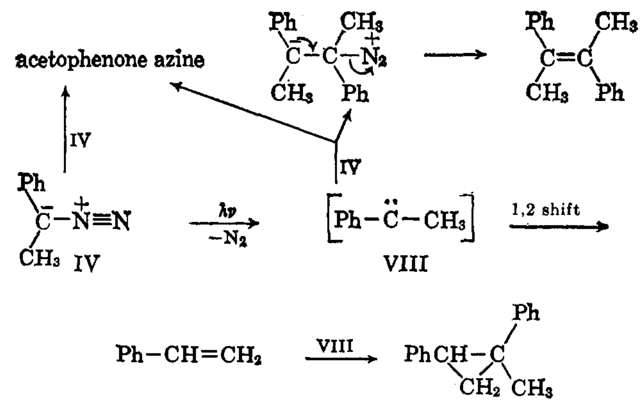


In the thermal decomposition of IV, the competition between the dimerization of the diazoalkane to acetophenone azine and the loss of nitrogen to give phenylmethylcarbene (VIII) seems to be the important factor. The overwhelming preference of the former (dimerization) may explain the sole formation of acetophenone azine ($k_3 >>> k_4$). The absence of any 2,3-diphenylbutane is, therefore, not surprising, since apparently VIII was not formed during thermal decomposition.



The formation of styrene during the photolysis of 1-phenyldiazoethane was significant, since, in this case, phenylmethylcarbene (singlet) must have been involved. Whether or not prior tautomerization to the diazirine (IV → III → VIII) took place cannot be ascertained from the present data. The large amount of acetophenone azine isolated mitigated against the possibility that styrene arose *via* the photolytic decomposition of the azine.[8] Furthermore, it has been shown that fairly high temperatures were required to convert azines to the corresponding olefins.[9] The absence of 2,3-diphenylbutane indicated that the triplet state carbene did not exist during the photolysis. The dimerization of 1-phenyldiazoethane (*vide supra*) probably contributed a very large extent to the formation of the azine. The various paths leading to the observed products are depicted in Scheme I.

SCHEME I



From the data presented, it can be concluded that the thermal decomposition of 1-phenyldiazoethane proceeded without the intermediacy of a divalent carbon; acetophenone azine arose solely *via* dimerization of the diazoalkane. The participation of a divalent carbon in the singlet state must have been involved in order to explain the formation of styrene during the photolytic decomposition of 1-phenyldiazoethane. No triplet state apparently was formed.

Experimental[10]

N-Benzylacetophenone Imine.—The general procedure used by Overberger, Marullo, and Hiskey[11] for the preparation of N-methylbenzylidene α-methylbenzylamine was followed. A mixture of 173.1 g. (1.44 moles) of acetophenone, 154.5 g. (1.44 moles) of benzylamine, 400 ml. of benzene, and 0.1 g. of *p*-toluenesulfonic acid was refluxed with stirring in a 2-l. flask equipped with a condenser and a Dean–Stark trap. After the theoretical amount of water had collected, the resulting yellow solution was cooled to 0° and washed with dilute solution of sodium bicarbonate and water until neutral. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed *in vacuo*. The residual viscous yellow oil then was distilled. After a forerun consisting mainly of acetophenone and benzylamine, 148 g. (49%) of a pale yellow liquid was collected at 125–126° (0.4 mm.). Upon standing overnight in the refrigerator, the product crystallized completely. Recrystallization from methanol–water (4:1) gave the pure product, m.p. 43–44°, lit.[12] m.p. 43.5–44.5°, prepared by condensation without removal of water and without solvent.

Attempted Synthesis of Phenylmethyl-1-diazacyclopropene[2] (Phenylmethyldiazirine).—To a mixture of 150 ml. of liquid ammonia and 240 ml. of methanol at −60° was added 83.9 g. (0.40 mole) of N-benzylacetophenone imine in 200 ml. of methanol. The mixture was stirred for 3 hr. and the temperature was allowed to rise to −30°. Then 54 g. (0.40 mole) of 85% hydroxylamine-O-sulfonic acid in 350 ml. of methanol, cooled to −10°, was added rapidly and the reaction mixture was stirred for 3 hr. at −30°. After that time, the cooling bath was removed and the reaction mixture was allowed to stand overnight. The residual oil obtained after filtration of the salts and removal of the solvents was dissolved in 1500 ml. of ether and dried over anhydrous sodium sulfate. Then excess powdered Dry Ice was added and the carbonate salt of benzylamine was collected. The solvent was evaporated *in vacuo* and, upon cooling, 1.5 g. of acetophenone azine, m.p. 120–121°, precipitated. Distillation of the oily filtrate through a 6-in. Vigreux column gave the separation shown in Table I.

TABLE I

Fraction (g.)	Temp., °C.	Pressure, mm.	Remarks
I (~1)	35–45	1.0	Reddish pink liquid which deposited some white crystals
II (~4)	45–86	0.9	Slight pinkish color
III (~0.3)	87–88	0.8	Slight amber color, crystallized in freezer, m.p. 39–40° (hydrazine)
IV (~5)	90–94	0.7	Colorless, crystallized upon standing, m.p. 57–59° (acetophenone oxime)

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[7] E. Schmitz, *Sitzber. Deut. Akad. Wiss. Berlin Kl. Chem. Geol. Biol.*, **6**, 23 (1962).

[8] C. H. Wang, *Proc. Chem. Soc.*, 309 (1961).

[9] H. E. Zimmerman and S. Somasekhara, *J. Am. Chem. Soc.*, **82**, 5865 (1960); C. G. Overberger and P. Chien, *ibid.*, **82**, 5874 (1960).

[10] All melting and boiling points are uncorrected.

[11] C. G. Overberger, N. P. Marullo, and R. O. Hiskey, *J. Am. Chem. Soc.*, **83**, 1374 (1961).

[12] G. Reddelien, *Ber.*, **53**, 338 (1920).

Fraction II was redistilled and gave a colorless liquid, b.p. 53–55° (3.7 mm.), main fraction. Upon standing in the light for 2 days, this colorless oil took on a pinkish tinge which deepened to a pinkish red. The infrared spectrum of the colorless oil was free of any absorption between 2600 and 2000 cm.$^{-1}$ while the reddish material had a strong band at 2042 cm.$^{-1}$; 1-phenyldiazoethane absorbs strongly at 2040 cm.$^{-1}$.

Thermal Decomposition of 1-Phenyldiazoethane.—To 75 ml. of refluxing benzene was added 100 ml. of a hexane solution of 1-phenyldiazoethane [prepared from 30 g. (0.22 mole) of acetophenone hydrazone and 60 g. (0.30 mole) of mercuric oxide[3]]. After 12 hr., the nitrogen evolution had stopped and the color of the solution had changed from deep red to yellow, indicating that complete decomposition had occurred. The yellow solution was dried over anhydrous sodium sulfate and the solvent was evaporated *in vacuo;* acetophenone azine, m.p. 119–120°, m.m.p. 119–121°, was collected with the aid of small portions of hexane. More azine was obtained from the successive filtrates until almost no color remained in the filtrate. Evaporation of the last filtrate gave trace amounts of acetophenone (identified by comparison of its infrared spectrum with that of an authentic sample) and benzoic acid; mixture melting point with a commercial sample was 120–122°.

Photolysis of 1-Phenyldiazoethane.—A solution of 1-phenyldiazoethane prepared from 47.4 g. (0.35 mole) of acetophenone hydrazone and 112 g. (0.52 mole) of mercuric oxide[3] in 330 ml. of hexane was photolyzed at 0–5° by means of a Hanovia high pressure mercury immersion lamp (200 watts). The progress of the reaction was followed by the evolution of nitrogen and the disappearance of the red color. When the red color had changed completely to canary yellow, the irradiation was stopped and the precipitated azine was collected. Further concentration of the resulting filtrates gave more acetophenone azine, m.p. 120–121°. A total of about 17 g. of azine was collected. The yellowish residue was taken up in 100 ml. of hexane and passed through a column of alumina; elution with hexane and benzene gave, after the removal of the solvents *in vacuo*, an almost colorless oil (~5 ml.). Distillation of this oil *in vacuo* gave a colorless liquid (~1.5 ml.), b.p. 80–81° (0.1 mm.). This clear oily liquid on standing crystallized almost completely as tiny needles, m.p. 105–106°. The n.m.r. of this solid in carbon tetrachloride solution had two sharp singlets at τ 2.71 (aromatic protons) and 8.03 (methyl protons). The spectrum was consistent with that expected for *trans*-α,α'-dimethylstilbene, m.p. 106–107°. The colorless filtrate was too small to be characterized conclusively. Its infrared spectrum had strong absorptions at 3058 and 1027 cm.$^{-1}$ (cyclopropane) and was almost identical with that of the product prepared by the addition of phenyldiazomethane to α-methylstyrene, followed by thermal decomposition of the intermediate 1-pyrazoline; the expected 1,2-diphenyl-1-methylcyclopropane was obtained as a colorless oil, b.p. 113–114° at 1 mm., but was contaminated by some olefin and the isomeric cyclopropane (*dl-cis* and *-trans* are possible here). From the Dry Ice trap used during the distillation was obtained a colorless liquid having a strong odor of styrene, positively identified by its infrared, ultraviolet, and n.m.r. spectra. Bromination of this liquid gave styrene dibromide, m.p. 74–75°. The residue from the distillation was examined and only small amounts of acetophenone azine and polymeric material were present. No 2,3-diphenylbutane could be detected.

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Derivatives of Sulfenic Acids. XLIV. The Kinetics of the Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with Phenylacetylene and 3-Hexyne[1]

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The rates of additions of 2,4-dinitrobenzenesulfenyl chloride (I) to phenylacetylene and 3-hexyne, in dry acetic acid at 45° and 55°, follow second-order kinetics, $-d(\text{ArSCl})/dt = k[\text{ArSCl}][\text{RC}{\equiv}\text{CR}']$. Addition of I to phenylacetylene is about 1/100th as fast as to styrene, while the addition to 3-hexyne is about 1/10th as fast as to cyclohexene. The addition of I to diphenylacetylene is also slower than are those of I to the stilbenes. Values for the activation energies and entropies of activation for the reactions of I with the acetylenes are given and compared with recorded values of these parameters for olefin additions. The rates of reactions of I with alkynes and alkenes are compared with available comparable data for bromine additions, and the need for further study of selected examples is noted. The structure of the adduct of I to phenylacetylene was shown to be $C_6H_5C(Cl){=}CH(SAr)$, where Ar = 2,4-dinitrophenyl, with a *trans* disposition of ArS and Cl groups assumed.

Earlier studies from this laboratory concerned additions of 2,4-dinitrobenzenesulfenyl chloride (I) to styrene,[2] *p*-substituted styrenes,[2a] and certain related compounds, including some symmetrical alkynes.[3-5] Studies of the reactions of I with cyclohexene were described by Hogg and Kharasch,[6] with *cis*- and *trans*-2-butene by Kharasch and Havlik,[7,8] with the *cis*- and *trans*-stilbenes by Slobodkin and Kharasch,[9] and with olefin oxides by Peters and Kharasch.[10] Related reactions with several olefins[11,12] and some bicyclic olefins[11-13] have also been examined.

For several additions of I to olefins, the kinetics of the reactions were investigated and the mechanism of addition to the carbon–carbon double bond was discussed.[2,6,9] Interest in the corresponding additions to the carbon–carbon triple bond prompted the present study. Phenylacetylene was selected because kinetic data are available for quantitative comparison with styrene, the corresponding olefin. Reaction rates for the addition of I to 3-hexyne were also determined, although quantitative data for the reaction with the corresponding olefin, 3-hexene, are not available.

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(1) This study was supported by grants from the National Science Foundation and the Office of Army Research (Durham).

(2) (a) W. L. Orr and N. Kharasch, *J. Am. Chem. Soc.*, **75**, 6030 (1953); (b) **78**, 1201 (1956).

(3) N. Kharasch and S. J. Assony, *ibid.*, **75**, 1081 (1953).

(4) N. Kharasch and S. J. Assony, *ibid.*, **77**, 3390 (1955).

(5) S. J. Assony and N. Kharasch, *Chem. Ind.* (London), 1388 (1954).

(6) D. R. Hogg and N. Kharasch, *J. Am. Chem. Soc.*, **78**, 2728 (1956); *cf.* D. S. Campbell and D. R. Hogg, *J. Chem. Soc.* (submitted).

(7) N. Kharasch and A. J. Havlik, *J. Am. Chem. Soc.*, **75**, 3734 (1953).

(8) A. J. Havlik and N. Kharasch, *ibid.*, **78**, 1207 (1956).

(9) N. R. Slobodkin and N. Kharasch, *ibid.*, **82**, 5837 (1960).

(10) D. Peters and N. Kharasch, *J. Org. Chem.*, **21**, 590 (1956).

(11) N. Kharasch and C. M. Buess, *J. Am. Chem. Soc.*, **71**, 2724 (1949).

(12) E. W. Malmberg and F. G. H. Lee, paper presented before the Organic Division, at the 127th National Meeting of the American Chemical Society, Minneapolis, Minn., April, 1955.

(13) H. Kwart and R. K. Miller, *J. Am. Chem. Soc.*, **78**, 5682 (1956).