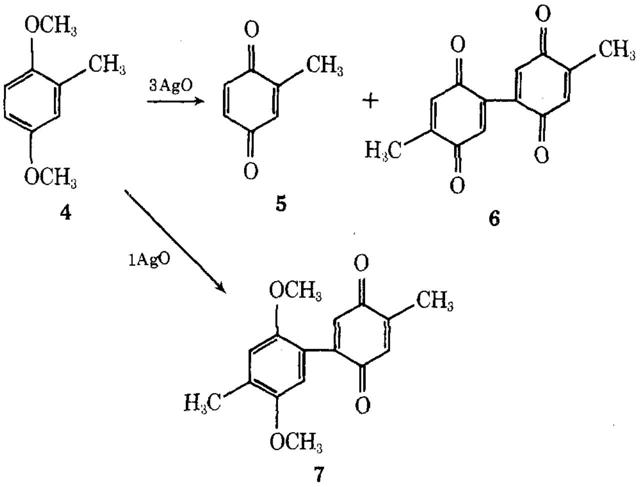
ported in the oxidation of 1,4-dimethoxybenzene and 2,5-dimethoxytoluene with ceric sulfate and a threefold increase in diquinone was observed with the latter,[4] suggesting that with electron-donating substituents arylation becomes a competing pathway.

The reduction of the electron-donating ability of the methyl group by introducing two acetoxy groups in 1 changed the reaction to cause exclusive demethylation. However, the fact that arylation occurs with 1,4-dimethoxybenzene if ceric sulfate is being used as oxidizing agent, while argentic oxide produced exclusively 1,4-benzoquinone, indicates that the oxidative demethylation reaction is sensitive to both the substituent and the oxidizing agent used.



4 5 6 7

Experimental Section

Oxidative Demethylation of 2,5-Dimethoxybenzaldehyde Diacetate (1).[3] To a suspension of 3.4 g (27.4 mmol) of AgO (supplied by Alfa Inorganics) in a solution of 2.1 g (7.8 mmol) of 1 in 80 ml of THF (freshly distilled over CaH_2) under stirring was added 8 ml of 6 *N* HNO_3, and after 3 min (by this time all AgO was dissolved) the reaction mixture was diluted with 160 ml of chloroform and 40 ml of water and stirred. The organic layer was separated, washed with water, dried (anhydrous $MgSO_4$), and evaporated to give 1.8 g of 2 (96%), mp 88–90°. By TLC examination (8:2 benzene–ether, silica gel plate) it was found to be pure. A recrystallized (2-propanol) sample had mp 90–92°; NMR ($CDCl_3$) δ 2.13 (s, 6, $OCOCH_3$), 6.83 (s, 3, 1,4-benzoquinone), 7.61 [s, 1, $CH(OAc)_2$]; ir ($CHCl_3$) 1666 (1,4-benzoquinone C=O), 1765 cm^{-1} (acetate C=O).

Anal. Calcd for $C_{11}H_{10}O_6$: C, 55.46; H, 4.23. Found: C, 55.37; H, 4.20.

Formation of Gentisaldehyde (3) from 2. A solution of 1.0 g (42 mmol) of 2 in 200 ml of ether was shaken with aqueous sodium dithionite in a separatory funnel until the ether layer turned colorless. The ether layer was separated, washed with water, and stirred with 50 ml of 1 *N* HCl for 2 hr (the reaction was followed by TLC, silica gel plates, 8:2 benzene–methanol). From the ether layer 0.4 g (69%) of gentisaldehyde was isolated, mp 90–92°. It was found to be identical with an authentic sample of 3.

Oxidation of 2,5-Dimethoxytoluene (4). A. The oxidation was carried out with 0.3 g (2 mmol) of 4 using 0.86 g (6 mmol) of AgO and 3 ml of 6 *N* HNO_3 following the procedure given for 1, which yielded 0.2 g of solid from which were separated by trituration with ether, followed by recrystallization (2-propanol), 0.1 g (42%) of 6, mp 189–190° (lit.[4] mp 178.5–179.5°), as an ether-insoluble component and 0.1 g (41%) of 5, mp 64–65°, as an ether-soluble component. 5 was compared with an authentic sample. 6 was confirmed based on its NMR spectrum ($CDCl_3$): δ 2.08 (d, 6, CH_3), 6.70 (m, 2, 1,4-benzoquinone, H adjacent to methyl group), 6.78 (s, 2, 1,4-benzoquinone, H adjacent to carbonyl group).

Anal. Calcd for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16. Found: C, 69.17; H, 4.10.

B. When 0.3 g of 4 was oxidized with 0.3 g (2 mmol) of AgO and 2 ml of 6 *N* HNO_3 in the manner described above, besides the unconverted 4 (separated by *n*-hexane trituration), 0.1 g (37%) of 7, mp 150–152°, was isolated, which melted at 154–155° after recrystallization from 2-propanol (lit.[5] mp 153°), NMR ($CDCl_3$) δ 2.03 (d, 3, CH_3 on quinone), 2.21 (s, 3, CH_3 on aromatic), 3.70 (s, 3, OCH_3), 3.73 (d, 3, OCH_3), 6.58 (m, 2, aromatic), 6.71 (m, 2, *p*-benzoquinone).

Registry No.—1, 55669-73-3; **2,** 55669-74-4; **3,** 1194-98-5; **4,** 24599-58-4; **5,** 553-97-9; **6,** 4388-07-2; **7,** 19965-46-9; silver oxide, 1301-96-8; sodium dithionite, 7775-14-6.

References and Notes

(1) C. D. Snyder and H. Rapoport, *J. Am. Chem. Soc.*, **94,** 227 (1972); **96,** 8046 (1974).

(2) H. Ulrich, D. V. Rao, B. Tucker, and A. A. R. Sayigh, *J. Org. Chem.*, **39,** 2437 (1974); we have also prepared gentisaldehyde from 2,5-dimethoxybenzaldehyde with 48% HBr in acetic anhydride at 100–105° for 6 hr in 60% yield.

(3) R. Preuss and R. Menzel, *Arch. Pharm.* (*Weinheim, Ger.*), **291,** 377 (1958); *Chem. Abstr.*, **53,** 5175*d* (1959).

(4) Y.-H. C. Giza, K. A. Kun, and H. G. Cassidy, *J. Org. Chem.*, **27,** 679 (1962).

(5) T. Posternak, W. Alcalay, R. Luzzati, and A. Tardent, *Helv. Chim. Acta*, **31,** 525 (1948).

Phenylcarbene from 3,5-Diphenyl-1-pyrazoline

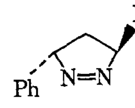
S. L. Buchwalter and G. L. Closs*

Chemistry Department, The University of Chicago,
Chicago, Illinois 60637

Received April 8, 1975

Thermal and photochemical extrusion of nitrogen from 1-pyrazolines has often been studied as a means of generating 1,3-diradicals.[1] In work directed toward observing such species,[2] we have recently noted an interesting alternate mode of decomposition in the case of *trans*-3,5-diphenyl-1-pyrazoline (1).

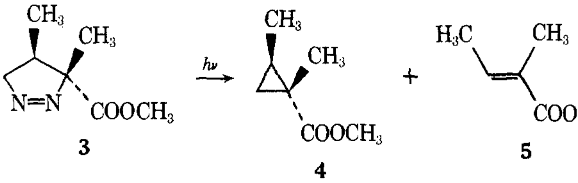
Previous workers[3-7] have suggested that retro-1,3-dipolar addition to give diazomethane (or a derivative) and an olefin may be a competing pathway of decomposition of some 1-pyrazolines. Thus, Rinehart and Van Auken[3] reported that irradiation of 3 gave methyl tiglate (5) as a side product in the formation of the cyclopropane (4). Their conclusion was that a reversal of the formation of 3 from 5 and diazomethane had occurred, although direct fragmentation to methylene, nitrogen, and olefin could not be ruled out. Similarly, it has been suggested, based on product analysis, that several bicyclic pyrazolines decompose by retro-1,3-dipolar addition.[4,5]



1

PhCHN$_2$

2



3 4 5

In the present case, direct evidence is adduced for a carbene-generating pathway in the photolysis of 1. A triplet ESR spectrum was observed when 1 was irradiated for short periods with ultraviolet light at 5.5 K either neat or in dilute toluene solution (see Table I). The spectrum from the neat sample was identical with the phenylcarbene spectrum obtained by irradiating phenyldiazomethane under the same conditions.[8] In addition to the carbene spectrum, the samples of 1 and 2 in toluene also gave weak spectra at-

Table I
ESR Absorptions[a]

Sample	Solvent	Absorptions, G[b]
1	Toluene	1640, 2200, 3035, 3170, 3420, 3535, 4870, 5860
1	Toluene-d_8	2200, 4870, 5860
1	Neat	2200, 3285,[c] 4870, 5860
2	Toluene	2200, 3140, 3210, 3370, 4870, 5860

[a] Microwave frequency 9.206 GHz. [b] In all samples except neat 1, a weak monoradical absorption at 3285 G was observed, which was also seen with toluene alone. [c] A strong monoradical absorption.

Table II
Analysis of Photolysis of 1

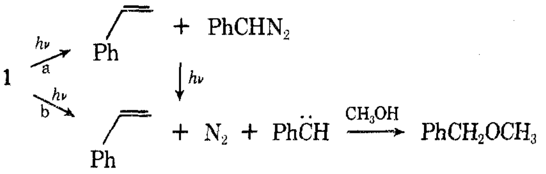
Compd	%[a]
Styrene	9 ± 2
Benzyl methyl ether	15 ± 3
cis-1,2-Diphenylcyclopropane	13 ± 1
trans-1,2-Diphenylcyclopropane	67 ± 4

[a] Disk integration corrected for relative response factors; low precision is due to tailing of methanol.

tributable to a triplet pair of benzyl radicals,[9] presumably formed by attack of phenyl carbene on the solvent. Significantly, the radical pair spectrum was absent when 1 was irradiated in toluene-d_8.

In order to assess the relative importance of carbene formation in the photolysis of 1, a trapping experiment was performed. The reaction was examined at room temperature with methanol serving as both solvent and carbene trap[10] (see Scheme I). A dilute solution of 1 in methanol was irradiated for 45 min, giving a mixture which was analyzed by VPC (Table II).

Scheme I



The results show that a minimum of about 10% of the photolysis proceeds to styrene and phenylcarbene. A considerably larger fraction of the reaction may actually follow this path, since it is unknown how much of the diphenylcyclopropanes result from addition of phenyl carbene to styrene. In fact, under conditions in which the olefin is a more reactive substrate than the reaction medium, the carbene pathway of decomposition may well go undetected. This possibility may explain why Overberger and Anselme[11] reported only diphenylcyclopropane as the product of photolysis of 1.

Present data cannot distinguish between a retro-1,3-dipolar addition (path a) and direct fragmentation (path b). A third possibility, that the carbene and styrene arise from the diphenylcyclopropanes, as is observed with shorter wavelength light,[10] is eliminated on the basis of control experiments. Regardless of whether path a or b is correct, it is clear that this alternate mode of decomposition is a complicating factor in the use of pyrazolines as diradical precursors. Although the generality of the carbene pathway is not known, its occurrence in 1 indicates that it must be considered in all cases before firm conclusions can be made about diradical species that may or may not be involved in the decomposition of 1-pyrazolines.

Experimental Section

Materials and Apparatus. *trans*-3,5-Diphenyl-1-pyrazoline[12] (1) and phenyldiazomethane[13] (2) were prepared by published procedures. A mixture of *cis*- and *trans*-1,2-diphenylcyclopropane was prepared by refluxing overnight a solution of 1 in benzene. Toluene was passed through a 1:1 mixture of alumina and silica gel prior to use. Toluene-d_8 (Stohler Isotope Chemicals) was used as received. Dilute toluene solutions (10% w/v, *ca.* 0.05 *M*) of **1**, **2**, and the mixture of cyclopropanes in 4 mm o.d. quartz tubing were degassed (three freeze–thaw cycles at 10^{-3} Torr) and sealed on a vacuum line.

A Varian E-9 spectrometer equipped with an Air Products and Chemicals Heli-Tran LTD-3-110 liquid helium transfer apparatus was used to record the ESR spectra. Gas chromatographic analysis was performed on a Varian Aerograph 1200 instrument equipped with a disk integrator. The column was 20% Carbowax 6000 on Chromosorb W, 6 ft × 0.125 in. at 80–180°.

Low-Temperature Photolyses. The samples were rapidly chilled in liquid nitrogen before being placed in the quartz dewar, which had been cooled to 5.5 K. A calibrated gold (0.07% iron) vs. chromel thermocouple sealed in a sample tube showed that the temperature at the sample varied from 5 to 6 K depending on the flow rate of helium.

The samples were irradiated for 5 min or less with a 2000-W mercury–xenon lamp operated at about 1300 W and filtered by water and Pyrex. Longer irradiation caused a reduction in the intensity of the spectra. The spectra are summarized in Table I. The sample containing the diphenylcyclopropanes gave no observable spectrum.

Room Temperature Photolyses. Samples of 1 and the diphenylcyclopropanes were dissolved in methanol (1% w/v, ~0.05 *M*) and placed in a water-jacketed Pyrex photolysis apparatus. Irradiation with a Hanovia medium-pressure 550-W lamp was continued for 45 min. In the case of the solution of 1, evolution of nitrogen was over in 35 min. The photolysis solutions were analyzed by gas chromatography (see Table II). Styrene and benzyl methyl ether were identified in the product mixture from 1 by coinjection of authentic samples on several different columns. A weighed mixture of styrene, benzyl methyl ether, and the diphenylcyclopropanes was also analyzed to calibrate the detector response. The irradiated diphenylcyclopropane solution did not contain styrene or benzyl methyl ether. In another experiment, a solution of 1 in methanol was refluxed for 24 hr. Only diphenylcyclopropanes were found in the product mixture.

Acknowledgment. Acknowledgment is made to the National Science Foundation (Grant GP-37481X) for support of this research.

Registry No.—**1**, 10514-16-6; **2**, 766-91-6; phenylcarbene, 3101-08-4.

References and Notes

(1) See, for example, R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **88**, 3963 (1966).
(2) G. L. Closs and S. L. Buchwalter, *J. Am. Chem. Soc.*, **97**, 3857 (1975).
(3) K. L. Rinehart, Jr., and T. V. Van Auken, *J. Am. Chem. Soc.*, **82**, 5251 (1960); **84**, 3736 (1962).
(4) M. Franck-Neumann, *Tetrahedron Lett.*, 2659 (1969).
(5) D. H. White, P. B. Condit, and R. G. Bergman, *J. Am. Chem. Soc.*, **94**, 1348 (1972); R. A. Keppel and R. G. Bergman, *ibid.*, **94**, 1350 (1972); D. F. Eaton, R. G. Bergman and G. S. Hammond, *ibid.*, **94**, 1351 (1972).
(6) D. E. McGreer and W. S. Wu, *Can. J. Chem.*, **45**, 461 (1967).
(7) R. Moore, A. Mishra, and R. J. Crawford, *Can. J. Chem.*, **46**, 3305 (1968).
(8) The carbene spectrum was similar to that reported previously; cf. A. M.

Trozzolo, R. W. Murray, and E. Wasserman, *J. Am. Chem. Soc.*, **84**, 4990 (1962).
(9) The radical pair spectra derived from **1** and **2** were not identical, which is consistent with previous observations by M. Trifunac; cf. M. Trifunac, Ph.D. Thesis, The University of Chicago, 1974.
(10) H. Kristinsson, K. N. Mehrotra, G. W. Griffin, R. C. Petterson, and C. S. Irving, *Chem. Ind. (London)*, 1562 (1966).
(11) C. G. Overberger and J.-P. Anselme, *J. Am. Chem. Soc.*, **86**, 658 (1968).
(12) J.-P. Anselme, *Org. Prep. Proced.*, **1**, 73 (1969).
(13) P. Yates and B. L. Shapiro, *J. Org. Chem.*, **23**, 759 (1958).

Synthesis of 7-Azanorbornene and *N*-Methyl-7-azanorbornene

Alan P. Marchand* and Robert W. Allen

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73069

Received March 19, 1975

A number of substituted 7-azanorbornanes,[1] 7-azabenzonorbornenes,[2,3] and 7-azanorbornadienes[4–8] have been reported. However, only one fully characterized *non*-ring-substituted 7-azanorbornene, *N*-phthalimido-7-azanorbornene, has been synthesized.[9] We now describe syntheses of 7-azanorbornene (**1**) and of the corresponding N-methylated amine (**2**).

In an earlier communication,[10] we reported the anomalous reduction of isolated carbon–carbon double bonds in *N*-carbethoxy-7-azanorbornene and in *N*-carbethoxy-2,3-benzo-7-azanorbornadiene by lithium aluminum hydride (or Vitride). In the present study, the successful synthesis of *N*-methyl-7-azanorbornene (**2**) was accomplished by diisobutylaluminum hydride reduction of *N*-carbethoxy-7-azanorbornene. The syntheses of **2** and of the parent (unsubstituted) amine (**1**), outlined in Scheme I, provide the first practical routes to the 7-azanorbornenyl system.

The starting material, *N*-benzyl-7-azanorbornadiene-2,3-dicarboxylic acid (**3**),[11] is obtained in 15–20% yield by Diels–Alder addition of acetylenedicarboxylic acid to *N*-benzylpyrrole.[12] Hydrogenation–hydrogenolysis of **3** affords **4**, which is then converted to the *N*-tosyl or *N*-carbethoxy derivative **5** and **6**. Electrolytic oxidative bisdecarboxylation of **5** and **6** gave the corresponding olefins **7** and **8**, which were further reduced to **1** and **2**, respectively.

Experimental Section

Melting points are uncorrected. NMR spectra were obtained on a Varian T-60 NMR spectrometer (Me_4Si internal standard). Ir spectra were obtained on a Perkin-Elmer Model IR-8 infrared spectrophotometer. Mass spectra were obtained on a Hitachi Perkin-Elmer Model RMU-7E mass spectrometer (70 eV); in order to obtain the molecular ion for compounds **1**, **2**, **7**, and **8**, it was necessary to cool the filament chamber to ambient temperature.

***N*-Carbethoxy-7-azanorbornane-*endo,endo*-2,3-dicarboxylic Acid (6).** *N*-Benzyl-7-azanorbornadiene-2,3-dicarboxylic acid[11] (**3**, 10.0 g, 36.9 mmol) was dissolved in excess aqueous sodium carbonate solution (100 ml). The resulting solution was hydrogenated (45 psig) over 10% palladized charcoal catalyst on a Parr apparatus. After 3 equiv of hydrogen had been taken up, the catalyst was removed by filtration. To the filtrate containing the hydrogenation product (**4**) was added excess ethyl chloroformate, and the resulting solution was stirred overnight at room temperature. The solution was then acidified with dilute aqueous hydrochloric acid and extracted with chloroform. The combined chloroform extracts were dried (Na_2SO_4), filtered, and then concentrated, affording **6** as a colorless syrup (8.20 g, 86.4%). Diacid **6** was characterized via the corresponding anhydride, **10**, which could be obtained via sublimation of syrupy **6** at 110° (0.1 mm). This procedure afforded **10** (5.80 g, 65.8%), which recrystallized from ether–hexane to afford colorless crystals: mp 111.5–112.8°; NMR ($CDCl_3$) δ 1.30 (t, $J = 6$ Hz, 3 H, $-OCH_2CH_3$), 1.61–2.1 (complex m, 4 H, 5,6-exo and endo ring protons), 3.73 (m, 2 H, 2,3-exo ring protons), 4.15 (q, $J = 6$ Hz, 2 H, $-OCH_2CH_3$), 4.70 [m, 2 H, 1,4 (bridgehead) protons]; ir (KBr) 2980 (w), 1860 (s), 1785 (s), 1690 (s), 900 cm^{-1} (s); mass spectrum *m/e* 239 (molecular ion), 141 (base peak), 140, 139, 122, 68.

Anal. Calcd for $C_{11}H_{13}NO_5$: C, 55.23; H, 5.48. Found: C, 55.30; H, 5.35.

***N*-Carbethoxy-7-azanorbornene (8).** Compound **6** (5.00 g, 19.5 mmol) was dissolved in an electrolysis solution which consisted of water (20 ml), triethylamine (2.5 ml), and pyridine (175 ml). A direct current (80 V, initial current 350 mA, Pt wire electrodes) was passed through this solution for 15 hr while the solution was maintained at 20° via external cooling. At the conclusion of the electrolysis, the current had dropped to 40 mA. The solution was then quenched with dilute, aqueous hydrochloric acid, and the resulting solution was extracted with diethyl ether (500 ml). The ether layer was then extracted with 10% aqueous sodium hydroxide solution to recover unreacted **6** (0.60 g). The ether layer was dried (Na_2SO_4), filtered, and then concentrated to afford crude **8**.

Scheme I