p-chlorophenyllithium[12] was employed instead of *m*-fluorophenyllithium.

1,2-Ethylenebis(tribenzylsilane). Benzylmagnesium chloride, prepared from 25.3 g. (0.20 mole) of benzyl chloride and 4.86 g. (0.20 g.-atom) of magnesium turnings in 200 ml. of diethyl ether, was added to a stirred solution of 5.9 g. (0.02 mole) of 1,2-ethylenebis(trichlorosilane)[13] in 55 ml. of diethyl ether. The mixture was refluxed for 12 hr., after which most of the solvent was distilled and replaced by xylene. Subsequent to refluxing at 100° for 50 hr., the mixture was hydrolyzed with 5% hydrochloric acid. Filtration gave 10.9 g. of crude product which was combined with 0.7 g. of similar material obtained by removal of the solvent from the dried organic layer. Three crystallizations of this solid from petroleum ether (b.p. 60–70°) and one crystallization from ethyl acetate afforded 10.2 g. (81%) of colorless crystals, m.p. 136–137°.

The first six compounds listed in Table III were prepared by a similar procedure from 1,2-ethylenebis-,[13] *m*-phenylenebis-,[13] or *p*-phenylenebis(trichlorosilane).[13] The compounds having long-chain alkyl groups, however, employed alkyllithium compounds which were prepared by a procedure similar to that used for *n*-butyllithium.[7]

4-Pentenyltriphenylsilane. The 4-pentenyllithium was prepared in 56% yield from 8.0 g. (0.054 mole) of 1-bromo-4-pentene in 70 ml. of diethyl ether and 0.9 g. (0.13 g.-atom) of lithium wire in 60 ml. of the same solvent at −30°.

A solution of 7.38 g. (0.025 mole) of chlorotriphenylsilane in 60 ml. of diethyl ether was added to this reagent at −30°. Subsequent to stirring at 0° for 15 min. and at room temperature for 11 hr., the mixture was hydrolyzed and worked up in the usual manner. Reduced pressure distillation at 155–157° (0.15 mm.), followed by crystallization from ethanol cooled by an ice bath, gave 5.6 g. (67%) of 4-pentenyltriphenylsilane, m.p. 45–46°.

Anal. Calcd. for $C_{23}H_{24}Si$: Si, 8.54. Found: Si, 8.61, 8.55.

1,5-Pentamethylenebis(triphenylsilane). a. *From 4-pentenyltriphenylsilane and triphenylsilane.* A mixture of 26 g. (0.10 mole) of triphenylsilane, 3.4 g. (0.01 mole) of 4-pentenyltriphenylsilane, 0.32 g. (0.0013 mole) of benzoyl peroxide, and 25 ml. of *n*-hexane was stirred at 80° for 20 hr., after which the excess triphenylsilane was distilled at 148–160° (0.7 mm.). A brown, gummy solid remained which was soluble in common organic solvents. Crystallization from a mixture of ethanol and methyl ethyl ketone gave 4.18 g. of product, m.p. 140–143°. Two additional crystallizations from an ethanol–ethyl acetate pair afforded 3.8 g. (65%) of pure product, m.p. 146–147°.

b. *From 1,5-pentamethylenedilithium and chlorotriphenylsilane.* To a solution of 1,5-pentamethylenedilithium (prepared from 20 g., 0.087 mole of 1,5-dibromopentane according to the procedure of West and Rochow[2]) in 180 ml. of diethyl ether was added, at −20°, 17.4 g. (0.059 mole) of chlorotriphenylsilane in 160 ml. of the same solvent. The mixture was allowed to warm to room temperature and to stir overnight. Hydrolysis and the usual work-up gave 8.4 g. (48%) of 1,5-pentamethylenebis(triphenylsilane), m.p. 145–146°. This product did not depress the melting point of the material obtained from the preceding experiment. Its analysis is reported in Table III.

3,3'-Biphenylenebis(triphenylsilane). A solution of 6 g. (0.019 mole) of 3,3'-dibromobiphenyl in 30 ml. of diethyl ether was added to 75 ml. of a stirred etherial solution of 0.038 mole of *n*-butyllithium at −30°. Subsequent to stirring at room temperature for 6 hr., and at reflux for 15 min., a solution of 11.3 g. (0.038 mole) of chlorotriphenylsilane in *ca.* 100 ml. of diethyl ether was added to the insoluble dilithium reagent. After refluxing for 45 min., 100 ml. of benzene was added and the mixture was distilled until the internal temperature reached 53°, at which temperature it was refluxed for 15 min. and then hydrolyzed. Filtration and recrystallization from a mixture of dioxane and water gave, in several crops, 8.85 g. (69%) of pure product, m.p. 221–223°.

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AMES, IOWA

(12) H. Gilman, W. Langham, and F. W. Moore, *J. Am. Chem. Soc.*, 62, 2327 (1940).

(13) Kindly furnished by Linde Air Products.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Fischer-Hepp Rearrangements of Substituted 9-Nitrosocarbazoles[1]

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Received July 21, 1961

Nitrosation of 1-bromocarbazole by conventional procedures led to a rearranged and oxidized product rather than to 1-bromo-9-nitrosocarbazole. Of the possible isomers, 1-bromo-3-nitrocarbazole, was synthesized unequivocally and identified with a product of the rearrangement-oxidation. Similarly, 1-isopropyl-4-methylcarbazole was nitrosated to 1-isopropyl-4-methyl-9-nitrosocarbazole, which rearranged readily to a mixture of 1-isopropyl-2 (or 3)-nitro-4-methylcarbazole and 1-isopropyl-4-methyl-6 (or 7)-nitrocarbazole.

DISCUSSION

Difficulties in nitrosating 1-substituted carbazoles in the 9- position were observed incidental to a study of preparation of asymmetrically substituted *N*-picryl-9-aminocarbazyl free radicals.[6] Two

(1) From the theses submitted to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the Ph.D. degree by H. J. S. Winkler (1959) and C. M. Kraebel (1959) and for the M. S. degree by T. D. Smith (1958).

(2) Deceased.

(3) P. L. Prof. G. Wittig, Org. Chem. Inst. d. Univ. Heidelberg, Tiergartenstrasse, Heidelberg.

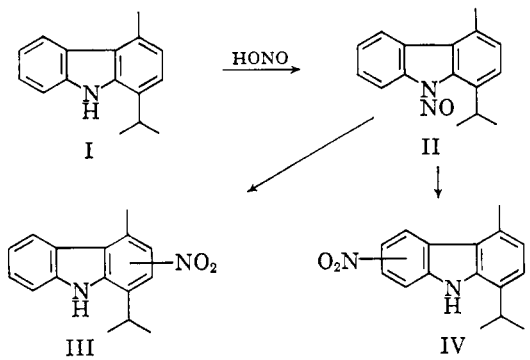
(4) B. F. Goodrich Co. Research Center, Brecksville 41, Ohio, to whom correspondence should be addressed.

(5) Monsanto Chemical Co., St. Louis 2, Mo.

examples of abnormal nitrosation are discussed; a bulky substituent, namely 1-bromo and 1-isopropyl, is involved in each case.

Nitrosation of substituted carbazoles, *e.g.*, 1-methyl, 1,2-benzo, 2-methyl, yielded the 9-nitroso derivative as expected when the reaction was carried out at sufficiently low temperatures, and the acetic acid used as solvent was removed carefully.[6]

1-Isopropyl-4-methylcarbazole (I) was nitrosated to 1-isopropyl-4-methyl-9-nitrosocarbazole (II), the structure of which was substantiated by the presence of N—O absorption[7] at 1480 cm.$^{-1}$ and the absence of N—H absorption in the 3500–3300-cm.$^{-1}$ region[8] of the infrared spectrum. A positive test for *N*-nitrosamines with Griess reagent[9] also supported the structural assignment.



Nitrosocarbazole II was stable under dry nitrogen for extended periods, but decomposed readily in the presence of light or air. Recrystallization from petroleum ether (b.p. 60–70°) in the presence of traces of acetic acid caused rearrangement to a mixture of nitrocarbazoles III and IV, which were separated by elution chromatography. The benzene eluate yielded a solid melting at 204–205°, which was assigned structure IV, 1-isopropyl-4-methyl-6-(or 7)-nitrocarbazole. The infrared spectrum of this compound lacked a band near 750 cm.$^{-1}$; this indicated the absence of an unsubstituted phenylene ring (see Table I). The band at 810 cm.$^{-1}$ suggests the presence of two adjacent hydrogens on an aromatic nucleus, while the absence of a band at 770 cm.$^{-1}$ precludes the presence of three adjacent hydrogens. Hence, the nitro group must be in the 6- or 7- position.

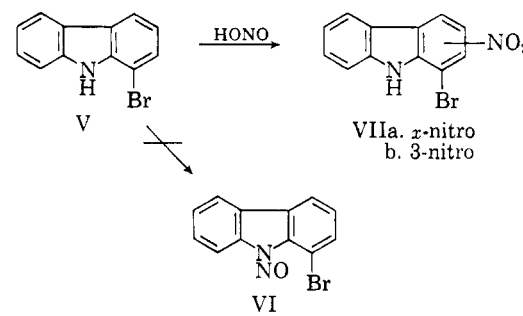
The ethyl acetate eluates yielded III, m.p. 210°. This substance was assigned the structure 1-isopropyl-3 (or 2)-nitro-4-methylcarbazole because its infrared spectrum, otherwise nearly identical with that of IV, has a peak at 740 cm.$^{-1}$ to indicate

TABLE I
INFRARED ASSIGNMENTS FOR SUBSTITUTED CARBAZOLES[7,8]

Cm.$^{-1}$	Assignment
3450	Normal N—H stretch for carbazoles
3350	N—H for carbazoles; low because of conjugation with nitro group
3100	Aromatic C—H stretch
3000–2800	Aliphatic C—H stretch (also Nujol)
1600 (1580)	Aromatic skeletal deformation
1510, 1300 (1520, 1330)	Aromatic nitro group
1480	N—O valence vibration
1440–1380 (1460, 1380)	Methyl and methylene vibration (also Nujol)
1380–1370	Isopropyl deformation
1330 (1300)	C—N vibration
1300 (1200–900)	Various C—H in-plane deformations
890 (860)	Single hydrogen on benzene nucleus
800 (810)	Two adjacent hydrogens on benzene nucleus
770	Three adjacent hydrogens on benzene nucleus
740 (750)	Four adjacent hydrogens on phenyl nucleus

the unsubstituted phenylene ring; the lack of a band near 810 cm.$^{-1}$ speaks against solely 1,4-disubstitution as in IV. The 3-nitro structure is preferred for III and the 6-nitro for IV owing to the tendency of aromatic *N*-nitrosamines to give *p*-nitroso derivatives on rearrangement.[10–12]

Conventional nitrosation procedures on 1-bromocarbazole (V) failed to give 1-bromo-9-nitrosocarbazole (VI). Attempts to prepare VI by direct nitrosation of V yielded only starting material under moderate conditions of temperature and reaction time (Table II, runs 1, 5–7, 10, 11). Under more vigorous conditions mixtures of 1-



bromo-*x*-nitrocarbazole (VIIa) and V were obtained (Table II, runs 2, 3, 12, 13). When nitrosation was conducted with cooling in glacial acetic acid (run 14), the product was mainly 1-bromo-3-nitrocarbazole (VIIb). Comparison of its melting point and infrared spectrum with those of an authentic sample of VIIb are the basis for this assignment. Of the isomeric compounds thought to arise, only the 3-isomer was prepared.

(6) H. J. S. Winkler, Ph.D. thesis, University of Maryland, 1959.
(7) C. E. Looney, *J. Am. Chem. Soc.*, **79**, 6136 (1957).
(8) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., John Wiley & Sons, Inc., New York, 1958.
(9) F. Feigl, *Spot Tests in Organic Chemistry*, 5th ed., Elsevier Publishing Co., New York, 1956, p. 153.
(10) O. Fischer and E. Hepp, *Ber.*, **19**, 2991 (1886); **20**, 1247 (1887).
(11) M. Ikuta, *Ann.*, **243**, 272 (1888).
(12) H. Wieland and H. Lecher, *Ann.*, **392**, 127, 156 (1912).

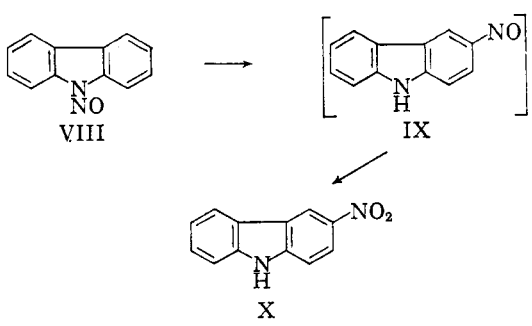
TABLE II

NITROSATION OF 1-BROMOCARBAZOLE

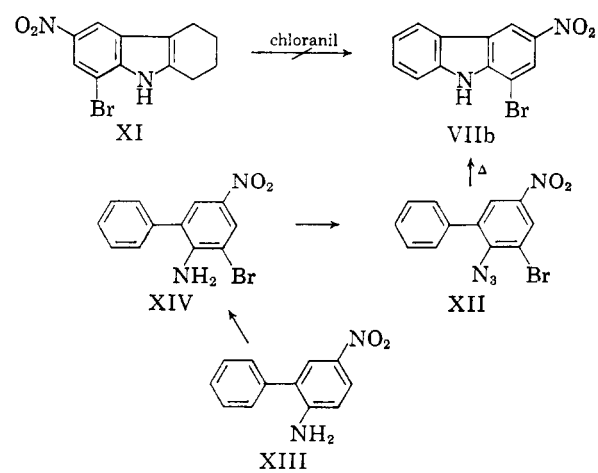
Run	Acid/Solvent	Time of Reaction	Temp.	Product(s)
1	HOAc/dioxane	10 min.	90–100°	Pale yellow crystals from CH_3OH, m.p. 122–123°[a]
2	HOAc/HOAc	1 hr.	Reflux	Yellow-brown needles from $C_2H_5OC_2H_3O$, m.p. 173–180°[b]
3	HOAc/HOAc	2 hr.	Reflux	Product not dried; used in run 4
4	HOAc/HOAc	5 min.	40–80°	Bright yellow needles, $CHCl_3$ insol.,[c,d] m.p. 234–242°; dull yellow needles from $CHCl_3$, m.p. 155–174°
5	HOAc/HOAc	10 min.	Reflux	Tan crystals from aq. C_2H_5OH, m.p. 121–122°[a]
6	HOAc/ether	8 hr.	25–30°	Cream crystals from dil. $C_2H_3O_2H$, m.p. 123–124°[a]
7	HOAc/EtOAc	30 min.	25–77°	White crystals from C_2H_5OH, m.p. 122–124°[a]
8	HOAc/HOAc	20 min.	90–100°	Yellow crystals, m.p. 175–>190°
9	Concd. H_2SO_4	10 min.	20–40°	Dark green amorphous mass; insol. in water or organic solvents
10	Concd. HCl/dioxane	30 min.	Below 10°	Pale yellow crystals from ether, m.p. 127–128°[a]
11	HOAc/HOAc	40 min.	90–100°	Pale yellow crystals from dil. C_2H_5OH, m.p. 124–125°[a]
12	HOAc/HOAc	2 hr.	90–100°	Bright yellow crystals from ether, m.p. 184–>210°; dull yellow crystals, m.p. 100–120°
13	HOAc/HOAc	4 hr.	Reflux	Bright yellow crystals, C_2H_5OH insol., m.p. 229–239°; yellow crystals from C_2H_5OH, m.p. 150–189°; yellow crystals from dil. C_2H_5OH, m.p. 117–130°
14	HOAc/HOAc	10 min.	10°	Yellow solid, m.p. 113–114°; yellow solid, m.p. 193–195°

[a] Mixed melting point with 1-bromocarbazole showed no depression. [b] Calcd. for 1-bromo-x-nitrocarbazole $C_{12}H_7BrN_2O_2$: C, 49.49; H, 2.41. Found: C, 49.56; H, 2.45. [c] Later purified to m.p. 244–245°. [d] Found: C, 49.61; H, 2.50.

The results described here appear closely related to the rearrangements discovered by Fischer and Hepp.[10] Among other examples[11] is the acid-catalyzed formation of *p*-nitroso-*N*-methylaniline from *N*-nitroso-*N*-methylaniline. The conversion of 9-nitrosocarbazole (VIII) to 3-nitrocarbazole (X) in low yield is probably an example of this process, which could involve the formation and oxidation of an intermediate C-nitroso compound (IX).[12] Neither this system nor the more complicated 1-substituted carbazole system has been investigated thoroughly.



The preparation of VIIb was attempted by dehydrogenation of 1,2,3,4-tetrahydro-6-nitro-8-bromocarbazole (XI) with chloranil, a method regularly used for preparation of substituted carbazoles.[13] Repeated treatments of XI with chloranil failed to yield VIIb. Dehydrogenation with platinum catalysts was not exploited because 1,2,3,4-



(13) B. M. Barclay and N. Campbell, *J. Chem. Soc.*, 532 (1945).

tetrahydro-8-bromocarbazole decomposed under these conditions. Hydrogenolysis has been reported under similar conditions.[14]

1-Bromo-3-nitrocarbazole (VIIb) was synthesized unequivocally in good yield by pyrolysis of 2-azido-3-bromo-5-nitrobiphenyl (XII), which was prepared as shown.

EXPERIMENTAL[15]

1-Isopropyl-4-methyl-9-nitrosocarbazole (II). To a cooled solution of 2.25 g. of 1-isopropyl-4-methylcarbazole[6] (I) in 45 ml. of glacial acetic acid (distilled from phosphorus pentoxide) was added 2.5 g. of sodium nitrite in 4 ml. of water while the reaction flask was cooled in ice water. A yellow solid separated after 10 min.; precipitation was completed by addition of 50 ml. of water. The solid was separated by filtration, thoroughly washed with water, and pressed dry. Recrystallization from petroleum ether gave II, m.p. 97–98°. The compound gave a positive test for *N*-nitroso with the Griess reagent.[9] Principal infrared maxima (10% solution in chloroform): 3100, 3000–2800, 1480, 1440–1380, 1380–1370, 1330, 1300 cm.$^{-1}$

1-Isopropyl-2(or 3)-nitro-4-methylcarbazole (III) *and 1-isopropyl-4-methyl-6(or 7)-nitrocarbazole* (IV). During attempted recrystallization from petroleum ether II containing residual acetic acid yielded a solid, m.p. 158–160°. Chromatography of this material on alumina gave a yellow solid melting at 204–205° (benzene eluates). Principal infrared absorption: 3420, 3050–2800, 1580 (1570), 1520 and 1310, 1460 and 1380, 1300, 1200–900, 810 cm.$^{-1}$ It was assigned structure IV.

Anal. Calcd. for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01. Found: C, 71.87, 71.92; H, 6.29, 6.28.

Elution with ethyl acetate gave a second fraction, m.p. 210°. This was designated 1-isopropyl-2(or 3)-nitro-4-methylcarbazole (III). Its infrared spectrum had strong bands at 3420, 3050–2800, 1580, 1520 and 1310, 1460 and 1380, 1200, 890 (or 860), and 740 cm.$^{-1}$

1-Bromocarbazole (V). A. *Catalytic dehydrogenation.*[16] Crude 1,2,3,4-tetrahydro-8-bromocarbazole, prepared according to a procedure of Barclay and Campbell[13] modified by Rogers and Corson,[17] was dissolved in redistilled *p*-cymene; 1.5 g. of 10% palladium-on-charcoal per gram of tetrahydrocarbazole was added, and the mixture was heated under reflux. In each of five trials the mixture foamed excessively, sometimes causing loss of material. The theoretical volume of hydrogen was not evolved when a closed collecting system was used.[18] A white solid, qualitatively identified as ammonium bromide, collected in cooler portions of the apparatus during an attempted dehydrogenation. This indicates that decomposition had occurred.

B. Dehydrogenation with chloranil.[13] Preparation of V in yields of 34–91% (based on distilled tetrahydro precursor) was achieved by this method. White flakes, m.p. 123–124°, were isolated by recrystallization from glacial acetic acid and from methanol followed by sublimation. The reported melting point is 111–112°.[13,19]

Anal. Calcd. for $C_{12}H_8BrN$: C, 58.56; H, 3.28; N, 5.69; Br, 32.5. Found: C, 58.62; H, 3.18; N, 5.82; Br, 32.3.

Nitrosation of V. A. General procedure (Table II, runs 1–13). A known weight (0.004–0.10 mole) of V was dissolved in the chosen solvent, and a slight excess of sodium nitrite (solid or aqueous solution) was added. The mixture was then heated to the desired temperature for the time shown. All products were isolated by crystallization. Infrared spectra are available for run 2 (m.p. 182–184°): 3450, 3000–2800, 1600, 1510 and 1300, 1460 and 1380, 800, 770, 740; run 4 (m.p. 244°): 3350, 3000–2800, 1600, 1510 and 1300, 1460 and 1380, 800–600 cm.$^{-1}$ The lack of distinguishing features in these spectra indicate that both samples are mixtures of 1-bromo-*x*-nitrocarbazoles.

B. *Run 14.* To a solution of 2.5 g. of V in 75 ml. of glacial acetic acid maintained at 10° was added a solution of 2.5 g. of sodium nitrite in 7.5 ml. of water over a period of 5 min. Water (100 ml.) was added after 10 min., and the resulting precipitate was recrystallized from petroleum ether. Chromatography of the material in 20 ml. of benzene on a 10-cm. column of alumina (Fisher A-540; 20 g.) gave unreacted V, m.p. 113–115° (benzene eluates) and a yellow solid, m.p. 193–195° (ethyl acetate eluates). The infrared spectrum of the latter was essentially identical with that of VIIb, m.p. 210–211°. A sample mixed with authentic VIIb melted at 203–204°.

2-Amino-5-nitrobiphenyl (XIII) was prepared following a published procedure.[20] In the nitration of 2-(*p*-toluenesulfonamido)biphenyl it was necessary to distill the acetic acid used as solvent from phosphorus pentoxide for good results.

2-Amino-3-bromo-5-nitrobiphenyl (XIV). The method of Smith and Brown[21] was used to prepare XIV in yields of 20–91%. The higher yields were realized with undried acetic acid as solvent. The *acetyl derivative* was prepared by shaking a solution of 0.50 g. of XIV in 10 ml. of acetic acid with 5 ml. of acetic anhydride and 1 ml. of concd. sulfuric acid and then pouring the mixture into ice water. Recrystallization from aqueous ethanol gave 0.42 g. (74%) of white solid, m.p. 181–182°.

Anal. Calcd. for $C_{14}H_{11}BrN_2O_3$: C, 50.17; H, 3.31; N, 8.36. Found: C, 50.09, 50.10, 50.11, 50.16; H, 3.62, 3.77, 3.29, 3.30; N, 8.16, 8.34.

2-Azido-3-bromo-5-nitrobiphenyl (XII)[22] was prepared by dissolving 1.0 g. of XIV in 20 ml. of undried acetic acid and 4 ml. of concd. sulfuric acid and cooling this mixture to 10°. Isoamyl nitrite (0.5 g., b.p. 97–100°), prepared immediately before use, was added all at once, and the resulting mixture was stirred for 1 hr. The mixture was diluted with 50 ml. of water; 0.3 g. of urea, and 0.5 g. of Darco were added. After 15 min. the green diazonium salt solution was separated from the solids by filtration. A solution of 0.5 g. of sodium azide in 10 ml. of water was added slowly (considerable gas evolution occurred) to the cooled solution. After slow warming to room temperature, the mixture was chilled to isolate the product. The crude was washed twice with 10% sodium carbonate solution and three times with water; it weighed 0.96 g. (88%) and turned rose-purple on standing in air. Recrystallization from ethanol–acetone gave straw-colored needles, m.p. 58–59°.

Anal. Calcd. for $C_{12}H_7BrN_4O_2$: C, 45.16; H, 2.21; Br, 25.04. Found: C, 45.34, 45.38; H, 2.12, 2.14; Br, 25.32, 25.42.

1-Bromo-3-nitrocarbazole (VIIb) A. *Attempted dehydrogenation of 1,2,3,4-tetrahydro-6-nitro-8-bromocarbazole* (XI).[18]

(14) J. Cummins and M. Tomlinson, *J. Chem. Soc.*, 3475 (1955).

(15) Melting points were taken in a Hershberg apparatus and are corrected. Boiling points are uncorrected. The infrared spectra were obtained on a Beckman IR-4 spectrophotometer, in Nujol mulls unless otherwise noted.

(16) E. C. Horning, M. G. Horning, and G. N. Walker, *J. Am. Chem. Soc.*, **70**, 3935 (1948).

(17) B. B. Corson and C. U. Rogers, *J. Am. Chem. Soc.*, **69**, 2910 (1947).

(18) In a control experiment 1,2,3,4-tetrahydrocarbazole was aromatized nearly quantitatively within 30 minutes under the same conditions.

(19) R. B. Carlin and G. W. Larson, *J. Am. Chem. Soc.*, **79**, 940 (1957) report the isolation of an unidentified monobromocarbazole, m.p. 124–125°. Presumably this is V.

(20) F. Case, *J. Am. Chem. Soc.*, **67**, 119 (1945).

(21) P. A. S. Smith and B. Brown, *J. Am. Chem. Soc.*, **73**, 2435 (1951).

(22) P. A. S. Smith and B. Brown, *J. Am. Chem. Soc.*, **73**, 2438 (1951). P. A. S. Smith *et. al.*, *Abstracts of Papers*, 123rd Meeting of the American Chemical Society, San Francisco, Calif., April 13–18, 1958, p. 61N.

Equimolar amounts of 2-bromo-4-nitrophenylhydrazine[23] and cyclohexanone were mixed for 5 min. in warm ethanol to form the cyclohexanone arylhydrazone; the resulting solution was added to an excess of 1:9 aqueous sulfuric acid. The acid mixture was heated under reflux for 6 hr. and then cooled. The precipitated cyclization product was recrystallized from ethanol to give yellow plates of XI, m.p. 227–234°. The tetrahydro compound was dissolved in sulfur-free xylene with the calculated amount of chloranil and heated under reflux until a test for unchanged chloranil was negative (24–48 hr. were required). The solvent and quinol were removed from the product, which was recrystallized from ethanol to yield yellow plates, m.p. 247–248° (XI).

Anal. Calcd. for $C_{12}H_7BrN_2O_2$(VIIb): C, 49.51; H, 2.42. Calcd. for $C_{12}H_{11}BrN_2O_2$(XI): C, 48.81; H, 3.73. Found: (run 1) C, 48.20; H, 3.83; (run 2) C, 48.16; H, 3.73; (run 3) C, 48.89; H, 3.73.

B. *Pyrolysis of* XII.[22] The carbazole was prepared by adding 1.5 g. of XII in small portions to 150 ml. of sulfuric acid-washed, distilled kerosene heated to 175–185°. Gas was evolved throughout the addition; after two additional min. at 175–185° the mixture was cooled and the olive-green solid which precipitated (1.05 g., 76%) was collected and recrystallized three times from ethanol. After sublimation the solid melted at 210–211°. Principal infrared absorption: 3350, 1600, 1520 and 1330, 1460 and 1380, 890, 750 cm.$^{-1}$

Anal. Calcd. for $C_{12}H_7BrN_2O_2$: C, 49.51; H, 2.42; N, 9.63. Found: C, 49.81, 50.01; H, 2.52, 2.48; N, 9.63.

(23) W. Davies, *J. Chem. Soc.*, 715 (1922).

Acknowledgment. We wish to thank Miss Jane Swan and Mrs. Kathryn Baylouney for the microanalyses, Mr. W. R. Feairheller, Jr., for his assistance in obtaining infrared spectra, and Professor E. R. Lippincott for his help in interpreting the spectra.

COLLEGE PARK, MD.

Notes

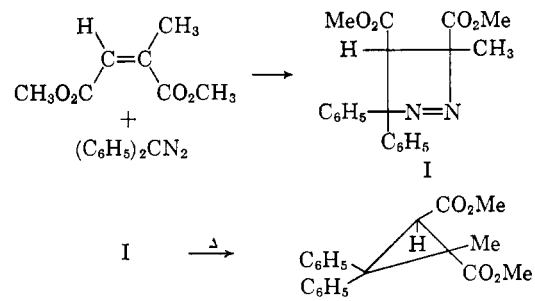
Pyrazolines. VI. The Stereochemistry of the Thermal Decomposition of 5,5-Diphenyl-1-pyrazolines[1]

W. M. JONES AND WUN-TEN TAI

Received September 21, 1961

For some time there has existed the idea that the thermal decomposition of 1-pyrazolines to their corresponding cyclopropanes occurs with a real degree of stereoselectivity.[2] However, as early as 1943, van Alphen[3] reported an observation which, when it came to our attention, caused us to doubt that the stereoselectivity of these decompositions was as general as had been presumed.[4]

Van Alphen found that the decomposition of the 1-pyrazoline resulting from the reaction diphenyldiazomethane with dimethyl citraconate gave a cyclopropane product in which the two carbomethoxy are *trans*. From this observation, the



obvious question requiring answer was whether this loss of stereospecificity occurred during the formation of the 1-pyrazoline or during its conversion to the cyclopropane. To report the results of an examination of this problem is the purpose of this note.

As van Alphen[3] reported a stable 1-pyrazoline from the reaction of dimethyl citraconate with diphenyldiazomethane, the obvious extension of his work which needed examination was the corresponding reaction with dimethyl mesaconate. This reaction was therefore effected and it was found that an excellent yield of a 1-pyrazoline was isolated. A sample of the material reported by van Alphen was then synthesized and it was found that the two 1-pyrazolines were, indeed, quite different. As these materials were quite stable to recrystallization conditions and neither showed

(1) For the previous paper, see W. S. Brey, Jr., and W. M. Jones, *J. Org. Chem.*, **26**, 1912 (1961). Based upon a thesis submitted by W. T. Tai in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) For example, see T. L. Jacobs in R. C. Elderfield, *Heterocyclic Compounds*, Wiley, New York, Vol. 5, 1957, p. 80; and the previous papers in this series.

(3) J. van Alphen, *Rec. trav. chim.*, **62**, 334 (1943).

(4) As we made this observation and after this work was begun, Rinehart and van Auken (see the Abstracts of Papers given at the American Chemical Society meeting in New York, September 11–16, 1960, p. 96P) reported an examination of the thermal decomposition of the two pyrazolines resulting from the reaction of diazomethane with methyl tiglate and methyl angelate. They found that these decompositions were nonstereospecific. This is most surprising in view of the similarity between their system and the two systems examined by von Auwers and Konig [K. von Auwers and F. Konig, *Ann.*, **496**, 252 (1932)].