Sublimation at 160–180 °C (0.1 mm) yielded 5.1 g (56%) of **2a**. An analytical sample was prepared by crystallization from CH_3OH: mp 243–244.5 °C (lit.[3,4] mp 236–238 °C); ^1H NMR (Me_2SO-d_6) δ 6.67 (1 H, d, J = 8 Hz), 7.47 (1 H, d, J = 8 Hz), 7.53 (1 H, dd, J = 4, 8 Hz), 8.53 (1 H, dd, J = 2, 8 Hz), 8.93 (1 H, dd, J = 2, 4 Hz), and 11.67 (1 H, bs, exchange).

Anal. Calcd for $C_8H_6N_2O$: C, 65.75; H, 4.14; N, 19.17. Found: C, 66.08; H, 4.43; N, 19.16.

The ether layer from above was dried, filtered, and evaporated to dryness. The residue was covered with C_6H_{14} and filtered to yield 2.4 g of crude **2b**. Sublimation at 70–80 °C (0.1 mm) gave 1.9 g (15%) of **2b**: mp 112–13 °C; ^1H NMR ($CDCl_3$) δ 7.63 (2 H, m), 8.5 (2 H, m), and 9.06 (1 H, dd, J = 2, 4 Hz). MS calcd for $C_8H_5BrN_2$: 207.9637. Found: 207.9635.

Preparation of 1-Hydroxy-2,7-naphthyridine (1a). Compound **1a** was prepared in a manner similar to **2a** from **4** (3.0 g, 0.017 mol), 30% HBr–HOAc (60 mL), and HOAc (30 mL) to yield 1.58 g (64%) of **1a**, sublimation 170–180 °C (0.1 mm). An analytical sample was prepared by crystallization from isopropyl alcohol: mp 260–62 °C (lit.[2] mp 255–62 °C); ^1H NMR (Me_2SO-d_6) δ 6.53 (1 H, d, J = 6 Hz), 7.43 (1 H, d, J = 6 Hz), 7.53 (1 H, d, J = 6 Hz), 8.67 (1 H, d, J = 6 Hz), 9.3 (1 H, s), and 10.83 (1 H, bs, exchange).

Anal. Calcd for $C_8H_6N_2O$: C, 65.74; H, 4.14; N, 19.17. Found: C, 65.49; H, 4.51; N, 18.78.

Preparation of 8-Hydroxy-1,7-naphthyridine (7a). Compound **7a** was prepared in a manner similar to **2a** from **9** (14.2 g, 0.082 mol), 30% HBr–HOAc (150 mL), and HOAc (75 mL) to yield 0.6 g (5%) of **7a**, sublimation 180–200 °C (0.1 mm). An analytical sample was prepared by crystallization from CH_3OH: mp 236–39 °C (lit.[8] 236–39 °C); ^1H NMR (Me_2SO-d_6) δ 6.50 (1 H, d, J = 6 Hz), 7.27 (1 H, d, J = 6 Hz), 7.67 (1 H, dd, J = 4, 8 Hz), 8.13 (1 H, dd, J = 2, 8 Hz), 8.60 (1 H, dd, J = 2, 4 Hz), and 11.5 (1 H, bs, exchange).

Anal. Calcd for $C_8H_6N_2O$: C, 65.74; H, 4.14; N, 19.17. Found: C, 66.13; H, 4.47; N, 19.39.

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Registry No.—**1a**, 67988-50-5; **2a**, 23616-31-1; **3**, 5444-01-9; **4**, 67988-51-6; **5**, 1721-23-9; **6**, 67988-52-7; **7a**, 67967-11-7; **8**, 20970-75-6; **9**, 67988-53-8.

References and Notes

(1) J. J. Baldwin, A. W. Raab, and G. S. Ponticello, *J. Org. Chem.*, **43**, 2529 (1978).
(2) N. Ikekawa, *Chem. Pharm. Bull.*, **6**, 269 (1958).
(3) T. J. Kress and W. W. Paudler, *Chem. Commun.*, 3, (1967).
(4) Y. Kobayashi, I. Kumadaki, and H. Sato, *Chem. Pharm. Bull.*, **17**, 1045 (1969).
(5) J. M. Bobbitt and D. A. Scola, *J. Org. Chem.*, **25**, 560, (1960).
(6) P. Baumgarten and A. Dornow, *Ber.*, **72B**, 563 (1939).
(7) H. Rozsa and B. Borivoje, *Ind. Chim. Belge*, **32**, 165 (1967).
(8) (a) S. M. Makin, A. A. Ismail, and M. I. Berezhnaya, *Zh. Org. Khim.*, **6**, 455 (1970); (b) S. M. Makin, O. A. Shavrygina, V. V. Mochalin, and M. I. Berezhnaya, *ibid.*, **5**, 2109 (1969).
(9) (a) A. Albert and A. Hampton, *J. Chem. Soc.*, 4985 (1952); (b) H. Rapoport and A. D. Batcho, *J. Org. Chem.*, **28**, 1753 (1963).
(10) Gratefully obtained from W. Halczenko of this laboratory.

Preparation and Photochemistry of Methyl 3,3,4-Triphenyl-3*H*-pyrazole-5-carboxylate

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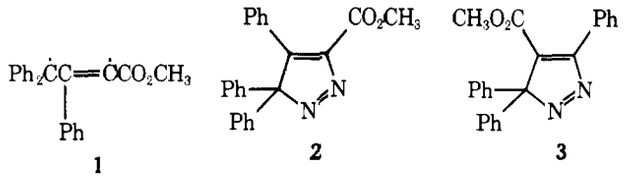
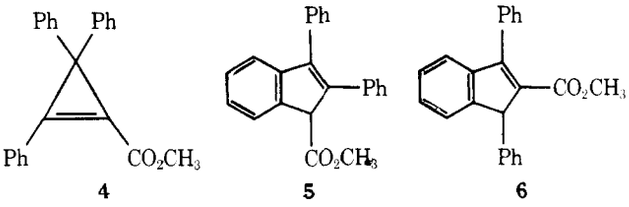
In order to study the reactivity of diradical **1**, we sought to generate it from the title compound **2**. Although van Alphen[1] had reported the synthesis of **2** from methyl 3-phenyl-2-propynoate and diphenyldiazomethane (DPDM), Hüttel and co-workers[2] later assigned structure **3** to the only



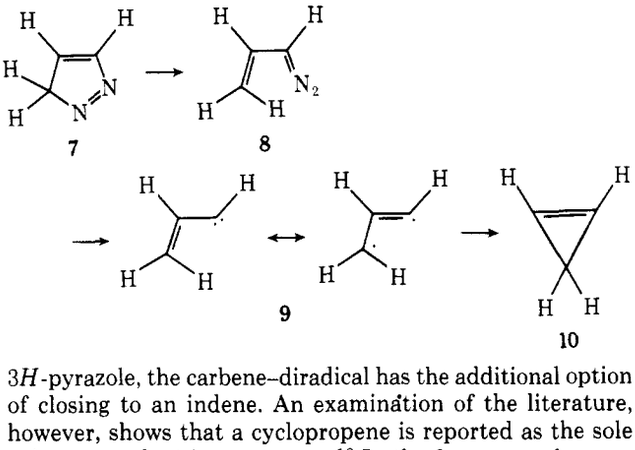
product isolated from this reaction. Their assignment was based on the observation that **3** underwent thermal rearrangement to a product that was then hydrolyzed and decarboxylated to the known 1,3,5-triphenyl-1*H*-pyrazole.[3]

We have now isolated both **2** and **3**, in a ratio of about 1:2, from the reaction of DPDM with methyl 3-phenyl-2-propynoate[4] and have unambiguously assigned their structures as follows. When a solution of **2** in benzene was irradiated through Pyrex for a short time, **4** and **5** were formed in a ratio



of about 1.2:1. Their properties matched those of authentic samples prepared by other routes.[5,6] When a solution of **3** was irradiated under these same conditions, **4** and **6** were formed in a ratio of about 1.3:1. An authentic sample of **6** was prepared from the corresponding acid, a known compound.[7] There was no change in **4** when it was irradiated under these conditions.

In general, the irradiation of a 3*H*-pyrazole (**7**) leads successively to the isomeric vinyl diazo compound **8**, to the vinyl carbene **9** after nitrogen loss, and finally to cyclopropene (**10**).[8,9] When a phenyl group is attached to position 3 of the



3*H*-pyrazole, the carbene–diradical has the additional option of closing to an indene. An examination of the literature, however, shows that a cyclopropene is reported as the sole primary product in most cases.[10] In the few cases where an indene is reported,[11] the irradiation was conducted under conditions known to isomerize cyclopropenes to indenes. The one exception[12] to this generalization is discussed below.

The simultaneous formation of cyclopropene and indene in the present case can be rationalized as a substituent effect on the multiplicity of **9**. A theoretical treatment[13] predicts that **8** leads initially to singlet carbene **9**, which may react or decay to triplet carbene **9** (14 kcal lower), which will then yield product. The relative energies of singlet and triplet **9** are apparently markedly affected by substituents; **11**, for example, shows an ESR signal, but **12** does not.[9] It may be that indene and cyclopropene come from different spin states of **9**: cyclopropene from the singlet and indene from the triplet. Al-

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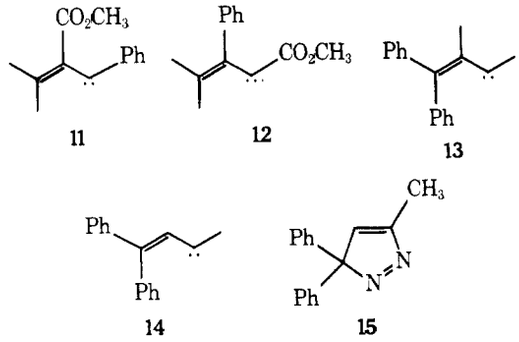

11 12 13 14 15

ternatively, Baron, Hendrick, and Jones[12] argue that the steric effect of substituents can affect the relative amounts of indene and cyclopropene from a given spin state. For example, triplet **13** (generated from the reaction of diphenylcarbene (DPC) and 2-butyne) yields mainly a cyclopropene, whereas **14** (from DPC and propyne) yields an indene exclusively. On the other hand, they also found that **14** formed by the irradiation of **15** gave cyclopropene and indene in a ratio of 2:1.

Experimental Section

General. Melting points are uncorrected. Infrared spectra were recorded in $CHCl_3$ solution on a Beckman IR-20-AX spectrometer, NMR spectra in $CDCl_3$ solution on a Varian T-60 spectrometer, and mass spectra at 70 eV on a Hitachi Perkin-Elmer double-focusing RMU-7 spectrometer. Irradiations were carried out using a 450 W Hanovia mercury arc in a quartz, water-cooled immersion well. In all cases, a Pyrex filter sleeve was inserted over the lamp inside the well. Nitrogen (purified by the method of Meites[14] and dried through a column of Drierite) was bubbled through the solution before and during the irradiation. Reagent benzene was distilled from potassium. Materials used in column chromatography were technical grade hexane and reagent grade benzene, distilled before use, Fisher alumina (80–200 mesh), and MCB silica gel (60–200 mesh).

Methyl 3,3,4-Triphenyl-3*H*-pyrazole-5-carboxylate (2) and Methyl 3,3,5-Triphenyl-3*H*-pyrazole-4-carboxylate (3). A mixture of 5.07 g (0.026 mol) of diphenyldiazomethane (DPDM), used without purification after its preparation by the method of Miller,[15] and 2.31 g (0.022 mol) of methyl 3-phenylpropynoate (**16**, prepared by refluxing a mixture of 10 g of 3-phenylpropynoic acid, 5 mL of concentrated H_2SO_4, and 100 mL of methanol for 7 h) was stored for 14 days in the dark. The NMR spectrum of the product, an orange oil weighing 7.0 g, showed three methoxy singlets, assigned to the two isomeric 3*H*-pyrazoles (**2**, at δ 3.88, relative area 1; and **3**, at δ 3.62, relative area 2) and to **16** (at δ 3.75, relative area 0.3). The aryl area (7.2–8.2) was about nine times greater than the total methoxyl area, the excess aryl area indicating the presence of benzophenone azine, which was isolated in varying yields from all reactions involving DPDM. The crude product was mixed with 4 mL of benzene and chromatographed on an alumina column (3 × 29 cm) that was slurry-packed in hexane: fractions 1 and 2 (125 mL each of hexane), 429 mg, DPDM; fraction 3 (100 mL of benzene), 404 mg; fraction 4 (100 mL of benzene), 5.055 g, **3** + azine; fraction 5 (100 mL of benzene), 316 mg; fraction 6 (100 mL of benzene), 250 mg, **2**; fractions 8–11 (100 mL of benzene each), 54, 86, 64, and 58 mg, all contained **2** and increasing amounts of materials with methoxy peaks near δ 3.6.

Repeated recrystallization of fraction 4 from methanol yielded **3**: mp 102–104 °C (lit.[1,2] mp 102 °C); NMR δ 8.2–7.1 (14 H, m, Ar) and 3.62 (3 H, s, OCH_3); IR 1725 cm^{-1} (C=O); mass spectrum, molecular ion at *m/e* 354.

Fraction 6 crystallized to an oily solid on standing. Initial attempts to purify this material by recrystallization from ether–hexane were unsuccessful. An attempt to purify it by rechromatographing it on alumina resulted in decomposition of the sample, perhaps by hydrolysis to the acid. (This result undoubtedly explains why the amount of **2** isolated by chromatography was less than that indicated in the NMR spectrum of the crude product.) Pure **2** was finally obtained from fractions 9 and 10 by washing the combined solid material with ether–hexane by decantation followed by several recrystallizations from hexane containing a little ether: mp 99–100 °C; ^1H NMR δ 7.4–7.1 (15 H, m, Ar) and 3.88 (3 H, s, OCH_3); IR 1725 cm^{-1} (C=O); mass spectrum, several minor peaks in the *m/e* 354 region, and major peaks at *m/e* 326 and 267 resulting from loss of N_2 and CO_2CH_3 from the parent; UV max (95% ethanol) 298 nm. Anal. Calcd ($C_{23}H_{18}N_2O_2$): C, 77.97; H, 5.09; N, 7.91. Found: C, 78.15; H, 5.25; N, 7.87.

Irradiation of 3. A solution of 0.05 g (0.0014 mol) of **3** in 100 mL of benzene was irradiated for 9 min. Solvent was evaporated at room temperature to yield an oil: 0.49 g; NMR δ 7.5–7.1 (m, Ar), 5.02 (s, methine), 3.87 (s, OCH_3 of **4**, relative area 4), and 3.47 (s, OCH_3 of **6**, relative area 3); IR 1720 (C=O) and 1820 (C=C of **4**) cm^{-1}. The separation of this mixture is best illustrated for another sample weighing 0.5 g, which contained roughly equal amounts of **4** and **6**. The oil was dissolved in 2 mL of benzene and chromatographed on a silica gel column (1.5 × 30 cm) slurry-packed in 10% benzene–90% hexane. The following were passed through the column before products were eluted: 100 mL of 10% benzene, 75 mL of 20% benzene, and 75 mL of 40% benzene. Pure **4** (0.17 g) was isolated from three 50-mL fractions of 60% benzene: mp 124–126 °C (lit.[5] mp 126 °C); NMR δ 7.5–7.1 (15 H, m, Ar) and 3.87 (3 H, s, OCH_3); IR 1830 (C=C) and 1720 (C=O) cm^{-1}; mass spectrum, molecular ion at *m/e* 326. Two intermediate fractions (50 mL of 60% benzene and 25 mL of 80% benzene) yielded 0.081 g of a mixture of **4** and **6**. Two 50-mL fractions (80% and 100% benzene) yielded 0.205 g of an oil which was almost pure **6**. Because this oil would not crystallize, it was rechromatographed on silica gel. The fractions eluted in 5% ether–hexane crystallized when hexane was added: mp 73–76 °C; NMR δ 7.46, 7.20 (14 H +, singlets, Ar), 5.04 (1 H, s, methine), and 3.54 (3 H, s, OCH_3); IR 1720 cm^{-1} (C=O); mass spectrum, molecular ion at *m/e* 326.

Irradiation of 2. A solution of 1.16 g (0.0033 mol) of **2** in 100 mL of benzene was irradiated for 9 min. The solvent was evaporated to yield an oil weighing 1.05 g: NMR δ 7.1–8.1 (m, Ar), 4.98 (s, methine), 3.85 (s, OCH_3, relative area 7.5), and 3.53 (s, OCH_3, relative area 6); IR 1830 (C=C) and 1720 (C=O) cm^{-1}. The oil was dissolved in 2 mL of benzene and chromatographed on a silica gel column (1.5 × 30 cm) slurry-packed in 10% benzene–90% hexane and eluted in 50-mL fractions as follows (fraction number, % benzene in solvent, weight of isolated material): 1, 10%, nil; 2, 10%, nil; 3, 20%, nil; 4, 40%, 43 mg; 5, 60%, 291 mg; 6, 60%, 192 mg; 7, 60%, 161 mg; 8, 60%, 70 mg; 9, 80%, 73 mg; 10, 80%, 30 mg; 11, 100%, 25 mg. According to NMR, fractions 4 and 5 were largely **4**, fractions 6 and 7 were mixtures of **4** and **5**, and fractions 8 and 9 were largely **5**. Crystalline material melting at 124–126 °C and having NMR, IR, and mass spectra identical with those of authentic **4** (see above) was isolated from fractions 4 and 5. Combined fractions 8 and 9 were recrystallized from hexane to yield crystals: mp 152–154 °C (lit.[6] mp 154–155 °C); NMR δ 7.2–7.5 (14 H, m, Ar), 4.98 (1 H, s, methine), and 3.57 (3 H, s, OCH_3); IR 1720 cm^{-1} (C=O); mass spectrum, molecular ion at *m/e* 326.

Preparation of Methyl 1,3-Diphenyl-2-indenecarboxylate (6). 1,3-Diphenylindene-2-carboxylic acid (**17**) was prepared by a modification of the method of Koelsch.[7] A mixture of 5 g (0.0187 mol) of 1,3-diphenylindene[16] and 8 mL (0.09 mol) of oxalyl chloride was refluxed for 70 h until gas evolution was very slow. Excess oxalyl chloride was removed on a rotary evaporator, and the residue was transferred in 20 mL of ether to an Erlenmeyer flask containing 10 g of sodium carbonate in 100 mL of water. This mixture was stirred for 1 h, 100 mL of water was added, and the mixture was boiled for 1 h. After it had cooled to room temperature, the aqueous solution was decanted from insoluble material and extracted with ether. The aqueous layer was acidified with concentrated HCl and then extracted with ether. The ether extracts were dried over Na_2SO_4 and evaporated to yield a yellow solid weighing 3.39 g. The NMR spectrum showed an aromatic multiplet between δ 7.2 and 7.5, a broadened singlet at δ 4.15, probably due to water, and two singlets at δ 5.24 and 5.07 with areas in the ratio of about 1:4, respectively. The singlet at δ 5.07 was assigned to the methine proton of **17**, and the singlet at δ 5.24 was assigned to the methine proton of 2-oxo-2-(1,3-diphenyl-2-indenyl)ethanoic acid (**18**). [A previous run (using the amounts described above) which was refluxed for 20 h yielded a mixture of **17** and **18**. When the mixture was recrystallized from glacial acetic acid, 170 mg of **18**, mp 216–217.5 °C, was isolated: NMR (acetone-d_6) δ 7.2–7.5 (14 H, three singlets, Ar), 5.22 (1 H, s, methine), and 4.15 (1.5 H, s, OH); mass spectrum, molecular ion at *m/e* 340. Treatment with diazomethane in ether yielded an oil: NMR δ 7.2–7.5 (14 H, three singlets, Ar), 5.15 (1 H, s, methine), and 3.17 (3 H, s, OCH_3); mass spectrum, molecular ion at *m/e* 354.] The mixture was dissolved in glacial acetic acid, and a solid melting at 196–201 °C was collected. It was recrystallized from benzene–hexane to yield 200 mg of white crystals: mp 203–203.5 °C [lit.[7] mp 194–196 °C]; NMR (acetone-d_6) δ 7.2–7.5 (14 H, m, Ar), 5.06 (1 H, s, methine), and 4.1 (1.5 H, broad, OH); mass spectrum, molecular ion at *m/e* 312. The acid dissolved in ether was converted to its methyl ester with diazomethane. The resultant oil crystallized only after chromatography on silica gel. Recrystallization from ether–hexane yielded white crystals, mp 75–77 °C. The NMR, IR, and mass spectra

were identical with those obtained on the sample prepared from **3**. Anal. ($C_{23}H_{18}O_2$). Calcd: H, 5.52. Found: H, 5.68.

Irradiation of Methyl 2,3,3-Triphenylcyclopropene-1-carboxylate (4). A solution of 0.18 g of **4** in 100 mL of benzene was irradiated for 9 min. Removal of solvent yielded 0.16 g of solid melting at 124–126 °C with IR and NMR spectra identical with those of **4**.

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Registry No.—**2**, 35313-60-1; **3**, 35313-61-2; **4**, 32379-25-2; **5**, 59099-81-9; **6**, 66442-72-6; **17**, 67845-24-3; **18**, 67845-25-4; DPDM, 883-40-9; methyl 3-phenylpropynoate, 4891-38-7; 1,3-diphenylindene, 4467-88-3; oxalyl chloride, 79-37-8.

References and Notes

(1) J. van Alphen, *Recl. Trav. Chim. Pays-Bas*, **62**, 485 (1943).
(2) R. Hüttel, J. Riedl, H. Martin, and K. Franke, *Chem. Ber.*, **93**, 1425 (1960); R. Hüttel, K. Franke, H. Martin, and J. Riedl, *ibid.*, **93**, 1433 (1960).
(3) The thermal and acid-catalyzed rearrangements of **3** (again the only isomer isolated) have been reexamined recently by M. I. Komendantov and R. R. Bekmukhametov, *Chem. Heterocycl. Compd. (Engl. Transl.)*, **11**, 68 (1976).
(4) Other examples of the formation of isomeric 3*H*-pyrazoles from the addition of substituted diazomethanes to substituted acetylenes have been reported: (a) M. Franck-Newmarin and C. Buchecker, *Tetrahedron Lett.*, 15 (1969); (b) G. E. Palmer, J. R. Bolton, and D. R. Arnold, *J. Am. Chem. Soc.*, **96**, 3708 (1974); (c) V. V. Razin, *J. Org. Chem. USSR (Engl. Transl.)*, **11**, 1441 (1975). See also ref 2.
(5) Cyclopropene **4** was prepared by the method of V. V. Razin and V. I. Gupalo, *J. Org. Chem. USSR (Engl. Transl.)*, **7**, 857 (1971).
(6) Indene **5** was prepared by the method of W. A. Pettit and J. W. Wilson, *J. Am. Chem. Soc.*, **99**, 6372 (1977). See also V. V. Razin and E. M. Rud, *J. Org. Chem. USSR (Engl. Transl.)*, **12**, 685 (1976).
(7) C. F. Koelsch, *J. Org. Chem.*, **25**, 2088 (1960).
(8) G. L. Closs, W. A. Böll, H. Heyn, and V. Dev, *J. Am. Chem. Soc.*, **90**, 173 (1968).
(9) D. R. Arnold, R. W. Humphreys, W. J. Leigh, and G. E. Palmer, *J. Am. Chem. Soc.*, **98**, 6225 (1976).
(10) (a) L. Schrader and W. Hartmann, *Tetrahedron Lett.*, 3995 (1973); (b) R. R. Bekmukhametov, *Sovrem. Probl. Khim, 1973*, 61 (1973); see *Chem. Abstr.*, **81**, 136042v (1974); (c) G. Snatzke and H. Langen, *Chem. Ber.*, **102**, 1865 (1969); (d) L. Schrader, *Chem. Ber.*, **104**, 941 (1971); (e) H. Dürr and L. Schrader, *Angew. Chem., Int. Ed. Engl.*, **8**, 446 (1969); (f) ref 3.
(11) (a) G. Ege, *Tetrahedron Lett.*, 1667 (1963); (b) G. Wittig and J. J. Hutchinson, *Justus Liebigs Ann. Chem.*, **741**, 79 (1970); (c) ref 4c.
(12) W. J. Baron, M. E. Hendrick, and M. Jones, Jr., *J. Am. Chem. Soc.*, **95**, 6286 (1973).
(13) J. H. Davis, W. A. Godcard, III, and R. G. Bergman, *J. Am. Chem. Soc.*, **99**, 2427 (1977).
(14) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).
(15) J. B. Miller, *J. Org. Chem.*, **24**, 560 (1959).
(16) K. Ziegler, H. Grabbe, and F. Ulrich, *Chem. Ber.*, **57**, 1983 (1924).

Properties of Cyclobutapyridines

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In a recent paper we reported the preparation and physical properties of a series of monoannelated pyridines in which a five- or six-membered ring is fused at either the 2,3 or 3,4 position of the pyridine ring. Also presented was a series of seven bisannelated pyridines in which all possible combinations of five- and six-membered rings are fused to the aromatic nucleus.[1] Just prior to the publication of this work, Trahanovsky and Riemann described the preparation of cyclobuta[*b*]pyridine (**1**) and cyclobuta[*c*]pyridine (**2**) via the vacuum pyrolysis of propargyl 4-pyridyl ether.[2] Utilizing their approach, these two isomeric pyridines have been synthesized and their properties will be herein discussed and compared with the systems examined earlier.

Table I compares the previously reported proton chemical shifts[3] for compounds **1** and **2** with those of higher homologues (**3–6**) as well as the analogous benzene derivatives (**7–9**). The carbon-13 chemical shifts of **1** and **2** are also presented in Table I. Peak assignments were made by analogy with higher homologues. The bridgehead carbon atoms always give the least intense peaks, and in the proton coupled spectrum they were shown to remain uncoupled.

The chemical shift of greatest interest is that of the aromatic carbon and attached proton located ortho to the point of ring fusion. In the benzene series the ortho aromatic proton (H-3) for benzocyclobutene is found to resonate at substantially higher field than what would be expected on the basis of simple rehybridization of the bridgehead carbon atom. This anomaly has also been pointed out in the case of the benzo[1,2:4,5]dicycloalkenes.[4] The ortho ring protons of **1** and **2** exhibit the same high field chemical shift which is nearly identical with the corresponding cyclohexene-fused analogues **4** and **6**. With the exception of C-2 for both cyclobutapyridines, all of the previously observed ^{13}C chemical shift trends are preserved. The bridgehead carbons move downfield while the pyridine carbon ortho to the bridgehead moves upfield with decreasing size of the fused ring. The failure of C-2 to follow these trends indicates that the electronegative effect of the adjacent nitrogen atom still plays an important role even though rehybridization effects can be transmitted through this heteroatom.

Table II records the basicities of **1** and **2** which were determined as half-neutralization potentials (HNP) by titration at 25 °C in acetic anhydride with 0.10 N perchloric acid in acetic acid. A well-established linear relationship between pK_a and HNP allows the calculation of basicities from a graph relating these values for a series of methyl-substituted pyridines.[5] A very dramatic decrease in basicity is observed for cyclobuta[*b*]pyridine (**1**) when compared to its higher homologues **3** and **4**. There is a comparable difference of almost 2 pK_a units between the positionally isomeric cyclobutapyridines, with the 3,4-fused system being decidedly more basic. In fact, the size of a ring fused at the 3,4 position has only a minor and apparently inconsistent influence on the basicity of the molecule. As was described in our earlier paper, Streitweiser's arguments for the rehybridization of bridgehead carbons can be invoked to explain the decrease in basicity of compound **1**.[6] The lone pair of electrons on nitrogen is held more tightly when that atom is bonded to a carbon atom using an orbital of higher s character.

The UV spectra of both cyclobutapyridines were measured in 95% ethanol: cyclobuta[*b*]pyridine (**1**) gave λ_{max} 269 nm (ϵ 4770), 272 (4800), and 278 (3420); and cyclobuta[*c*]pyridine (**2**) gave λ_{max} 253 nm (ϵ 1740), 258 (1950), and 263 (1620). These absorptions occur at about the same energies as were observed for the next higher homologues **3** and **5**. While the extinction coefficients for **2** are nearly identical with those observed for the other 3,4-fused systems **5** and **6**, a regular trend of increasing extinction coefficients is observed for the series **4**, **3**, **1**. For the bisannelated pyridines discussed previously,[1] a similar trend is clearly evident for the para-fused systems. It therefore appears that the extinction coefficient of pyridine is more sensitive to effects resulting from ring fusion at the position adjacent to the nitrogen atom.

Both **1** and **2** were observed to undergo catalytic hydrogenation at room temperature and 1 atm of hydrogen, utilizing either palladium on charcoal or platinum oxide as the catalyst. When a mixture of **1** and **2** was hydrogenated, the 2,3 isomer (**1**) was seen to reduce just slightly faster than the 3,4 isomer (**2**). The resulting azabicyclo[4.2.0]octanes **10** and **11** were purified by preparative VPC and identified by their spectral properties. These two isomers represent the last two unreported azabicyclooctanes.[8] Under identical reduction conditions, a mixture of 2,3- and 3,4-lutidine was totally unreactive.

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