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**.

Acknowledgment. Partial support of this research by the Research Corporation is gratefully acknowledged.

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.

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Properties of Cyclobutapyridines

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Received July 5, 1978

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.

0022-3263/78/1943-4882$01.00/0

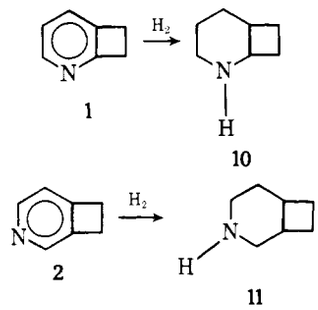
Table I. Proton and Carbon-13 Chemical Shifts[a] for the Aromatic Ring of Monoannelated Pyridines and Benzenes

Compd	no.	H_2	H_3	H_4	H_5	H_6	C_2	C_3	C_4	C_5	C_6
	1			7.32	7.10	8.39	164.2	140.2	129.6	122.9	148.6
	3[b]			7.47	7.00	8.31	165.3	136.8	132.0	120.8	147.0
	4[b]			7.31	6.98	8.31	157.1	132.1	136.7	120.7	146.4
	2	8.16			6.92	8.39	147.8	142.4	155.3	118.2	142.7
	5[b]	8.44			7.14	8.33	147.1	139.9	153.3	119.7	145.7
	6[b]	8.27			6.94	8.24	150.3	132.8	145.9	123.7	146.3
	7[c]		6.90	6.76			145.6	122.1	126.6		
	8[c]		7.07	6.99			144.0	124.4	126.2		
	9[c]		7.07	7.07			137.0	129.2	125.2		

[a] $CDCl_3$ solutions; reported in parts per million relative to internal Me_4Si. [b] Reference 1. [c] Reference 7.

Table II. Basicities of Monoannelated Pyridines

compd	pK_a
cyclobuta[*b*]pyridine (**1**)	4.85
2,3-trimethylenepyridine (**3**)	5.95
5,6,7,8-tetrahydroquinoline (**4**)	6.65
cyclobuta[*c*]pyridine (**2**)	6.75
3,4-trimethylenepyridine (**5**)	6.96
5,6,7,8-tetrahydroisoquinoline (**6**)	6.83



Experimental Section

Propargyl 4-Pyridyl Ether *N*-Oxide. To 50 mL of propargyl alcohol, cooled with an ice bath and under nitrogen, was added 1.35 g (0.06 mol) of sodium cut into small pieces. When the sodium dissolved, 7.0 g (0.05 mol) of 4-nitropyridine *N*-oxide was added in one portion and the mixture was refluxed for 3 h. The unreacted propargyl alcohol was distilled at 50 °C under reduced pressure, and the residue was dissolved in about 50 mL of water and neutralized with concentrated HCl. The water was removed on a rotary evaporator, and the residue was dried under vacuum and digested with two 100-mL portions of chloroform. Evaporation of the chloroform afforded 7.0 g of a yellow solid. This crude material gave a satisfactory NMR spectrum: ($CDCl_3$) δ 8.11 (d, 2, J = 7.5 Hz, H_2 and H_6), 6.87 (d, 2, J = 7.5 Hz, H_3 and H_5), and 4.70 (d, 2, $-C{\equiv}CH$). The *N*-oxide proved to be very hydroscopic and thus was used in the next step without further purification.

Propargyl 4-Pyridyl Ether. To a mixture of 10 g (0.074 mol) of propargyl 4-pyridyl ether *N*-oxide in 125 mL of chloroform at 0 °C was added dropwise 20 mL of phosphorus trichloride. After addition was complete, the reaction mixture was allowed to come to room temperature and refluxed for 1 h. The mixture was then cooled, poured onto ice, and made basic with concentrated ammonium hydroxide. This solution was extracted with chloroform, and the combined extracts were dried over potassium carbonate. Evaporation of the solvent yielded a material which was recrystallized from 1:1 chloroform–hexane to give 6.5 g (74%) of propargyl 4-pyridyl ether, mp 77–78 °C (lit.[2] mp 77–77.5 °C).

Cyclobutapyridines (1 and 2). Vacuum pyrolysis [600 °C (10^{-2}–10^{-4} mm)] of 1–2-g portions of propargyl 4-pyridyl ether according to the method of Trahanovsky[2,9] afforded ~50% yields of a mixture of **1** and **2**. The crude pyrolysis product was first purified by Kugelrohr distillation at 40 °C (4–5 mm), after which the two isomers were separated by preparative gas chromatography on a $\frac{3}{8}$ in. × 15 ft column of 10% Carbowax 20M and 10% KOH on Chromsorb W, 60–80 mesh, at 95 °C and 100 mL/min. The retention times of **1** and **2** were 30 and 34 min, respectively. Their physical properties are presented in the text above.

2-Azabicyclo[4.2.0]octane and 3-Azabicyclo[4.2.0]octane. To a solution of 0.40 g (3.8 mmol) of a 2:1 mixture of **1** and **2**, respectively, in 30 mL of methanol was added 20 mg of 10% palladium on charcoal. The mixture was hydrogenated at room temperature and atmospheric pressure for 16 h, after which time VPC analysis ($\frac{1}{8}$ in. × 15 ft column of 10% Carbowax 20M + 5% KOH on Chromosorb W, 80–100 mesh, at 130 °C and 30 mL/min) showed the disappearance of peaks at 6.5 and 7.5 min, corresponding to **1** and **2**, and the appearance of two new peaks at 2.3 and 2.6 min in a ratio of 2:1, respectively. The catalyst was removed by filtration, and the methanol was evaporated to yield 0.35 g of an oil from which the two new peaks were isolated pure by preparative VPC. The shorter retention time peak was identified as 2-azabicyclo[4.2.0]octane (**10**): 100 MHz NMR (C_6D_6) δ 3.44 (q, 1, J = 7 Hz, bridgehead C_1-H), 2.5–2.95 (m, 2, C_3-H), 1.86–2.32 (m, 3), 1.70–1.86 (m, 4, C_7-H and C_8-H), 1.35–1.60 (m, 2), and 1.18 (s, 1, NH); IR (thin film) 3290, 2940, 2870, 1450, 1335, and 1320 cm^{-1}. Treatment with picric acid yielded the corresponding picrate, mp 115–116 °C.

Anal. Calcd for $C_{13}H_{16}N_4O_7$: C, 45.89; H, 4.74; N, 16.46. Found: C, 45.88; H, 4.44; N, 16.53.

The longer retention time peak was identified as 3-azabicyclo[4.2.0]octane (**11**): 100 MHz NMR (C_6D_6) δ 2.51–3.00 (m, 4, C_2-H and C_4-H), 2.22–2.46 (m, 2, C_1-H and C_6-H), 1.82–2.00 (m, 4, C_7-H and C_8-H), 1.4–1.76 (m, 2, C_5-H), and 0.99 (s, 1, NH); IR (thin film) 3295, 2930, 1465, and 1312 cm^{-1}. Treatment with picric acid yielded the corresponding picrate, mp 121 °C.

Anal. Calcd for $C_{13}H_{16}N_4O_7$: C, 45.89; H, 4.74; N, 16.46. Found: C, 45.56; H, 4.61; N, 16.74.

To ensure the correct assignments of **10** and **11**, 30 mg of pure **2** was hydrogenated under the same conditions as described above until the single VPC peak at 7.5 min had been completely converted to a peak at 2.6 min, which upon isolation showed an IR spectrum that was identical with that of **11**.

Basicity Measurements. Basicities were determined according

to the method of Markgraf and Katt[10] by potentiometric titration with a Radiometer RTS622 Recording Titration System fitted with a glass indicator electrode and a saturated calomel reference electrode, previously equilibrated with acetic anhydride for 48 h. Titrations were carried out at 25.00 ± 0.05 °C under a nitrogen atmosphere in a water-jacketed cell connected to a constant temperature bath and fitted with a neoprene cover drilled to accommodate two electrodes, a buret, thermometer, and nitrogen inlet tube. In a typical run, an accurately weighed amount of the pyridine derivative (ca. 5×10^{-4} mol) was dissolved in acetic anhydride in a nitrogen-swept 25-mL volumetric flask; a 10-mL aliquot was transferred to the titration cell, diluted with 60 mL of acetic anhydride, and with magnetic stirring titrated with 0.10 N perchloric acid in acetic acid (Fisher No. SO-P-339, ca. 3.5 mL). The end point and half-neutralization potential were determined graphically. All runs were carried out in duplicate, with a precision of ±2 mV.

Acknowledgment. Financial support from the Robert A. Welch Foundation is gratefully acknowledged. The Varian XL-100 NMR spectrometer was obtained with a major equipment grant from the National Science Foundation.

Registry No.—1, 56911-25-2; 2, 56911-27-4; 3, 533-37-9; 4, 10500-57-9; 5, 533-35-7; 6, 36556-06-6; 10, 278-33-1; 11, 327-60-6; propargyl 4-pyridyl ether *N*-oxide, 67858-39-3; propargyl 4-pyridyl ether, 64818-18-4; proparyl alcohol, 107-19-7; 4-nitropyridine *N*-oxide, 1124-33-0.

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Ramberg–Backlund Sulfur Extrusion from 2-Carboethoxy Sulfones

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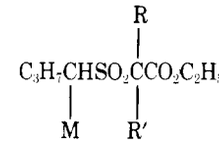
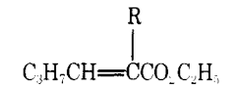
Received February 14, 1978

Previous studies in our laboratory have established an efficient ring expansion route to 2-carboethoxythiacycloalkenes of variable ring size.[1] In this note, we describe a simple procedure for conversion of the ring expansion products into carbocycles by Ramberg–Backlund sulfur extrusion. The method employs the convenient chlorinating agent hexachloroethane,[2] which is compatible with NaH or $KOC(CH_3)_3$ and can be used in a one-pot Ramberg–Backlund process.

In a simple example of the one-pot reaction, the α-methyl sulfone ester **1** reacts with excess NaH and 1.2 mol of C_2Cl_6 (DME solution, 20 °C) to give ethyl 2-methylhex-2-enoate (**2**) in 54% isolated yield (1:1 *E*/*Z*). Similar treatment of the unsubstituted sulfone ester **3** affords an α-chloro derivative **4** (60% isolated, not optimized), but **4** does not undergo Ramberg–Backlund sulfur extrusion upon treatment with various bases. This observation suggests that **4** is converted into the enolate **5**, which is strongly favored relative to **6**, the anion required for episulfone formation. In the absence of an enolizable hydrogen, eipsulfone formation can occur. Thus, treatment of **4** with excess C_2Cl_6 and sodium hydride results in slow formation of ethyl 2-chlorohex-2-enoate (**7**) (*E*,*Z* mixture) via α-dichloro sulfone ester **8**.



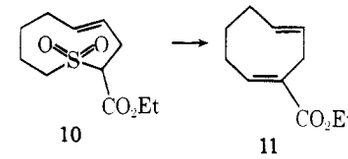
1, R = CH_3; R′ = M = H
3, R = R′ = M = H
4, R = Cl; R′ = M = H
5, R = Cl; R′ = Li; M = H
6, R = Cl; R′ = H; M = Li
8, R = R′ = Cl; M = H
9, R = CH_3; R′ = Cl; M = H



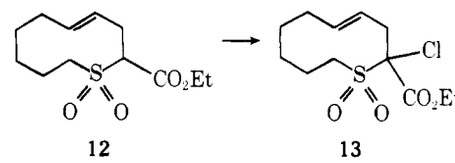
2, R = CH_3
7, R = Cl

The one-pot Ramberg–Backlund conditions described above have been optimized for sulfur extrusion from the nine-membered sulfone ester **10**. After 3 h at 20 °C, the novel *cis,trans*-cyclooctadiene ester **11** can be isolated in 75% yield by distillation of the crude product. In support of structure **11**, the NMR spectrum shows two hydrogens of a disubstituted trans double bond (J_{vinyl} = 16 Hz), the β proton of an unsaturated ester (6.7 ppm), and a doubly allylic methylene ABX pattern centered at 3.0 ppm. A characteristic *trans*-cyclooctene infrared band at 985 cm^{-1} is further evidence for structure **11**. Analogous sulfur extrusion from the ten-membered ring **12** is considerably slower. After 24 h at 20 °C, 33% of the cyclononadiene **14** (IR 988 cm^{-1}; NMR 6.96 ppm, unsaturated ester β-H) was isolated, together with 54% of α-chloro sulfone **13**. Prolonged reaction with sodium hydride favors **14** at the expense of **13**. Starting with purified **13**, a more rapid conversion can be achieved with potassium *tert*-butoxide and gives a 50% isolated yield of **14**.

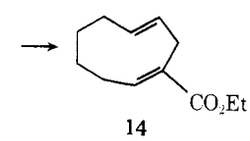
Under the usual conditions (1.2 equiv of C_2Cl_6, NaH), the 12-membered sulfone ester **15** affords a complex mixture of products. This mixture has not been characterized in detail, but the crude NMR spectrum retains only a fraction of the expected carboethoxy signals. When the experiment is performed using excess C_2Cl_6 and potassium *tert*-butoxide as base, the major isolable product (35%) also lacks the carboethoxy group. According to NMR and mass spectral evidence,



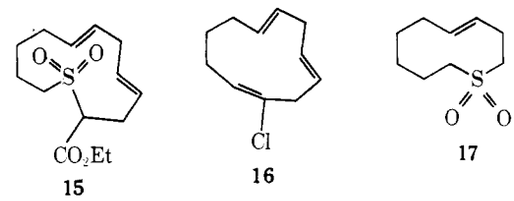
10 **11**



12 **13**



14



15 **16** **17**

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