washed with water, dried, and evaporated to afford either liquid or solid product. The physical and spetroscopic characteristics are given in Tables II and III.

General Procedure for the Aldol Reactions. A solution of 0.017 mol of LDA in 20 mL of THF was cooled to −78 °C and a solution of **1a** in 10 mL of THF was added. The solution became orange and was stirred at −78 °C for 30 min. The electrophile (0.017 mol) in 10 mL of THF was added and the solution stirred at −78 °C for 3–4 h. The reaction was quenched without warming by the addition of saturated NH_4Cl, allowed to warm to room temperature, and acidified with 10% HCl, and the organic material was extracted into ether (3 × 50 mL). The extracts were washed with 10% HCl and water, dried, and evaporated before distillation or recrystallization. The physical and spectroscopic properties of the products are given in Tables II and III.

Acknowledgment. The financial support of the Natural Sciences and Engineering Research Council of Canada in the form of operating grants and a scholarship (to P.M.) made this work possible. We would like to thank Dr. P. M. Beaumier for the GC/MS results at a critical time in the work.

Registry No. **1a**, 35350-46-0; **1b**, 60822-65-3; **2a**, 87602-19-5; **2b**, 88802-41-9; **2c**, 88802-42-0; **2d**, 88802-43-1; **2e**, 88802-44-2; **2f**, 88802-45-3; **2g** (isomer 1), 88802-46-4; **2g** (isomer 2), 88802-47-5; **2h** (isomer 1), 88802-48-6; **2h** (isomer 2), 88825-33-6; **2i** (isomer 1), 88802-49-7; **2i** (isomer 2), 88802-50-0; **2j** (isomer 1), 88802-51-1; **2j** (isomer 2), 88802-52-2; **2k**, 88802-53-3; **2l**, 88802-54-4; **2m** (isomer 1), 88802-55-5; **2m** (isomer 2), 88802-56-6; **2n** (isomer 1), 88802-57-7; **2n** (isomer 2), 88802-58-8; **2o** (isomer 1), 88802-59-9; **2o** (isomer 2), 88802-60-2; **3b**, 88802-61-3; **4b**, 88802-62-4; CH_3I, 74-88-4; $PhCH_2Br$, 100-39-0; $CH_2{=}CHCH_2Br$, 106-95-6; $CH_3(CH_2)_3I$, 542-69-8; CH_3CHO, 75-07-0; PhCHO, 100-52-7; $CH_2{=}CHC(O)CH_3$, 78-94-4; Me_2CO, 67-64-1; cyclohexenone, 930-68-7; thiolactic acid, 79-42-5.

One-Step Synthesis of 3,8-Methano-1-aza[10]annulene Derivatives via Diels–Alder Reaction of Benzocyclopropene with 1,2,4-Triazines[1]

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A new approach to the synthesis of 3,8-methano-1-aza[10]annulene derivatives based on the Diels–Alder reaction of benzocyclopropene with electron-deficient 1,2,4-triazines was developed. The exceptionally electron-deficient triazines **4a** and **4b** yielded azaannulenes **6a** and **6b** under normal conditions, while the less activated triazines **4c** and **4d** required ultrahigh pressure (15 kbar) to produce annulenes **6c** and **6d**. Both the disubstituted and monosubstituted annulenes **6c** and **6d** were quite unstable. The cyanoannulene **6b** was, however, converted into other stable annulene derivatives including the 2,9-disubstituted compound **6j**.

3,8-Methano-1-aza[10]annulene (1), as yet not synthesized, is a bridged methylene homologue of isoquinoline.

1

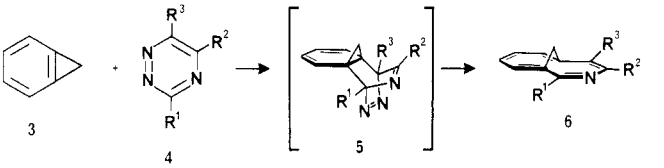
The preparation of annulene **1** and derivatives thereof is of interest in order to study the physical properties and reactions of this class of heterocycles. Moreover, the substitution of this bridged heterocyclic system for the isoquinoline moiety of natural products and medicinal agents would lead to novel structures with potentially interesting biological activities.

Recently, the synthesis of some 10-alkoxy-3,8-methano-1-aza[10]annulenes **2** was independently achieved by three groups of investigators.[2] Unfortunately, further

2 ; R = CH_3, C_2H_5

study of these novel heterocycles was hampered by the lengths and low overall yields of the published synthetic routes. We have also reported preliminary studies on a novel, one-step synthesis of carboxylic ester derivatives of this class of annulenes, which provided the opportunity for preparing substantial quantities of these substances.[3] We now describe in more detail the preparations, physical properties, and reactions of these heteroannulenes.

Scheme I



a, R^1,R^2,R^3 = CO_2Et
b, R^1 = CN; R^2,R^3 = CO_2Et
c, R^1 = H; R^2,R^3 = CO_2Et
d, R^1 = CO_2Et; R^2,R^3 = H
e, R^1 = CO_2K; R^2,R^3 = CO_2Et
f, R^1 = CO_2H; R^2,R^3 = CO_2Et
g, R^1 = CO_2Me; R^2,R^3 = CO_2Et
h, R^1 = OEt; R^2,R^3 = CO_2Et
i, R^1 = CN; R^2 = CO_2H; R^3 = CO_2Et
j, R^1 = CN; R^2 = H; R^3 = CO_2Et

Results and Discussion

Prior to our investigations of azaannulene synthesis, several reports on the synthesis of pyridines from 1,2,4-

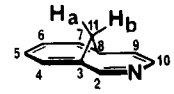
(1) Contribution no. 177 and 658 from the Institutes of Bio-Organic Chemistry and Organic Chemistry, respectively.

(2) Lipa, W. J.; Crawford, H. J.; Radlick, P. C.; Helmkamp, G. K. *J. Org. Chem.* **1979**, *43*, 3813. Schäter-Ridder, M.; Wagner, A.; Schwaborn, M.; Schreiner, E.; Devrout, E.; Vogel E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 853. Gölz, H. J.; Muchowski, J. M.; Maddox, M. L. *Ibid.* **1978**, *17*, 855.

(3) Maddox, M. L.; Martin, J. C.; Muchowski, J. M. *Tetrahedron Lett.* **1980**, *21*, 7.

0022-3263/84/1949-1040$01.50/0

Table I. ^{1}H NMR Spectral Data of 3,8-Methano-1-aza[10]annulenes[a]



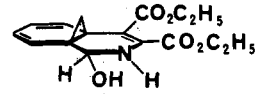
		δ								
no.	MHz	H-2	H-4	H-5	H-6	H-7	H-9	H-10	H-11a	H-11b	$J_{11a,b}$, Hz
6a	300		8.37	7.20	7.27	7.87			0.34	−0.35	9.4
6b	300		7.94	7.25	7.32	7.87			0.49	−0.18	9.4
6c	90	8.37	7.58	7.10	7.24	7.81			0.18	−0.09	9.1
6d	360		8.29	7.18	7.23	7.42	7.32	8.47	−0.11	−0.36	9.4
6g	90		8.42	7.2	7.2	7.87			0.38	−0.35	9.2
6h	300		7.25	6.90	7.03	7.21			−0.01	1.26	8.6
6i	360		7.79	7.40	7.43	7.95			0.43	−0.20	9.4
6j	360		7.85	7.30	7.43	8.31		9.33	0.18	−0.26	9.4
7	100		6.65	6.65	6.65	6.85			1.2	1.2	

[a] The vicinal coupling constants along the aromatic periphery were all approximately 9 Hz except for $J_{9,10}$ = 6 Hz for **6d**. H-11b was assigned to the bridgehead proton showing an additional long-range coupling of approximately 1 Hz. The spectrum of the hydrate **7** was not sufficiently well-enough resolved in order to assign coupling constants.

triazines via Diels–Alder reaction with various dienophiles had appeared.[4,5] Additionally, literature precedent existed for the ability of benzocyclopropene **3** to participate as a dienophile in Diels–Alder reactions.[6] On the basis of this background, it occured to us to investigate an approach to azaannulenes depicted in Scheme I. The expectation was that benzocyclopropene would react with 1,2,4-triazines **4** to yield annulenes **6** via tetracyclic intermediate **5**. This cycloaddition should proceed with inverse electron demand, indicating that more electron deficient triazines would give the more facile reaction;[6] thus, this reaction was investigated with triazines substituted with electron-withdrawing groups.

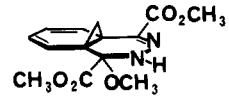
In fact, the highly electron-deficient triazines **4a**[7] and **4b** were sufficiently activated to react thermally (55 °C) with an equal molar amount of benzocyclopropene[8] **3** in ethyl acetate/hexane to yield annulenes **6a** (67%) and **6b** (70%). Following chromatographic purification, these compounds were isolated as stable yellow crystalline solids. Less activated triazines **4c** and **4d** did not react with benzocyclopropene under these conditions. Additionally, attempts to force the thermal reaction with higher temperatures failed because above 80 °C benzocyclopropene rapidly dimerizes to 9,10-dihydrophenanthrene.[6b]

In order to extend the scope of this reaction, the use of ultra high pressure to accelerate the cycloaddition was explored.[9] This proved successful, and triazines **4c**[7] and **4d**[10] reacted with benzocyclopropene at a pressure of 15 kbar (55 °C) to furnish annulenes **6c** (41%) and **6d** (33%), respectively, as oils following chromatographic purification. 1,2,4-Triazine[11] failed to react even under ultra high pressure, demonstrating a requirement for at least one electron-withdrawing activating functionality. Annulene **6d** was very unstable and decomposed within 1 month at 0 °C. Disubstituted annulene **6c** proved to be moderately sensitive upon exposure to air. Isolation by column chromatography was satisfactory, but purification by preparative thin-layer chromatography afforded hydrate **7**. The norcaradiene structure for **7** was indicated by its



7

^{1}H NMR spectrum; vida infra. This type of reaction has also been noted by Korte and Vogel who found that a 4,8-methano-1,2-diaza[10]annulene formed an addition compound **8** with methanol.[6a]



8

Additional chemical studies were carried out on trisubstituted heterocycles **6a** and **6b** with the goal of preparing other annulene derivatives. Selective hydrolysis of **6a** with 1 equiv of KOH yielded, as an intermediate, carboxylic acid salt **6e**. The corresponding carboxylic acid **6f** proved to be too unstable to isolate by simple extraction of **6e** from dilute HCl but could be prepared by brief treatment with Dowex 50W-X8 and characterized by conversion to methyl ester **6g** with diazomethane. Decarboxylation of **6e** was achieved by reaction with oxalyl chloride and then *tert*-butyl hydroperoxide followed by heating the resulting perester at reflux in xylene. Hydrate **7** was isolated in only 7% yield by preparative thin-layer chromatography.

Cyanoannulene **6b** was more amenable to chemical modification. For instance, the cyano group in **6b** was displaced by ethoxide on treatment with ethanolic KOH, giving **6h** as an oil in 88% yield. Alternatively, the less hindered ester functionality of **6b** was saponified (KOH, H_2O, THF) to furnish acid **6i** in quantitative yield. In contrast to **6f**, carboxylic acid **6i** was an easily isolated, stable crystalline substance. Moreover, simple heating of **6i** resulted in decarboxylation to yield disubstituted annulene **6j** as an oil in 57% yield. The regioselectivity of the ester hydrolysis of **6b** was confirmed by examination of the ^{1}H NMR spectrum of **6j**. The absorption of proton

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(5) More recently the utility 1,2,4-triazines as pyridine synthons has been investigated by us and others. (a) Martin, J. C. *J. Org. Chem.* **1982**, *47*, 3761. (b) Boger, D. L.; Panek, J. S. *Ibid.* **1981**, *46*, 2179. Boger, D. L., Panek, J. S. *Ibid.* **1983**, *48*, 621.

(6) (a) Korte, S. Dissertation, Universitat Köln, 1968. (b) Halton, B. *Chem. Rev.* **1973**, *73*, 113. (c) Benzocyclopropene was recently shown to react with mesoionic compounds. Kato, H.; Toda, S. *J. Chem. Soc., Chem. Commun.* **1982**, 510.

(7) Rätz, R.; Schroeder, H. *J. Org. Chem.* **1958**, *23*, 1931.

(8) Billups, W. E.; Blakeney, A. J.; Chow, W. Y. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 12. A hexane solution of benzocyclopropene was used in all cases. The concentration of benzocyclopropene in this solution was determined by ^{1}H NMR.

(9) For a review on the utility of ultra high pressure in organic synthesis, see: Gladysz, J. A. *CHEMTECH* **1979**, 373.

(10) Paudler, W. W.; Barton, J. M. *J. Org. Chem.* **1966**, *31*, 1720.

(11) Krass, D.; Paudler, W. W. *Synthesis* **1974**, 351.

H-10 appeared as a sharp singlet and that of H-11a a sharp doublet. If the proton had been at position 9 instead of 10, an additional long-range coupling of approximately 1 Hz would have been noted.[12]

The ^1H NMR spectra of these annulenes (Table I) are consistent with the delocalized aromatic structure.[2,12] The bridging the methylene proton absorptions are far upfield in the range of δ 0.49 to −0.36, which indicates considerable shielding of these protons by the aromatic ring current. Additionally, the downfield protons of the aromatic periphery absorb at the expected frequency range downfield of δ 7.0, which is typical of an aromatic system. Also noteworthy is that the geminal coupling of the methylene protons is approximately 9 MHz, which supports the delocalized structural assignment. Moreover, the delocalized nature of the unsaturation is indicated by equivalent vicinal coupling constants ($J_{4,5} = J_{5,6} = J_{6,7} = 9$ Hz) on the unsubstituted portion of the annulenes. In contrast, the norcaradiene structure for hydrate **7** is supported by the absorptions of the olefinic protons at δ 5–6 and the bridging methylene protons at δ 1.2.

Experimental Section

Nuclear magnetic resonance spectra were recorded on Varian A-60 (^1H NMR, 60 MHz), Bruker WH-90 (^1H NMR, 90 MHz and ^{13}C NMR, 22.62 MHz), Varian HA-100 (^1H NMR, 100 MHz), Bruker WM-300 (^1H NMR, 300 MHz), and Nicolet 360 (^1H NMR, 360 MHz) spectrometers from samples dissolved in deuteriochloroform, and chemical shifts are reported in parts per million downfield from internal tetramethylsilane. Ultraviolet spectra were recorded on a Cary 14 spectrometer from samples dissolved in methanol. Infrared spectra (IR) were recorded on a Perkin-Elmer 247B instrument. Mass spectra (MS) were recorded on a Finnigan MAT CH7 spectrometer operating in the direct inlet mode. The high-resolution mass spectrum was recorded on a Varian MAT 311A spectrometer. Spectroscopic data were obtained by the Syntex Analytical Research Division. Some elemental analyses were obtained from Dr. A. Bernhardt, Elbach uber Engelskirchen, Germany. Melting points were determined on a Fischer-Johns apparatus and are uncorrected.

3-Cyano-5,6-dicarbethoxy-1,2,4-triazine (4b). To a solution of diethyl dioxosuccinate[13] (25.2 g, 0.125 mol) in toluene (250 mL) under Ar at 75 °C was added cyanoformamidrazone[14] (10.5 g, 0.125 mmol). The solution was heated quickly to reflux, and water was removed via a Dean–Stark trap. After 30 min at reflux, the solution was evaporated and the residue distilled on a Kugelrohr apparatus (bp 120–150 °C (1 torr)) to give a dark brown oil. The distillate was crystallized from ethyl acetate/hexane to afford 5.5 g (18%) of **4b**: mp 75–76 °C; ^1H NMR (60 MHz) δ 4.60 (q, J = 7 Hz, 2 H, CH_2), 4.57 (q, J = 7 Hz, 2 H, CH_2), 1.47 (t, J = 7 Hz, 3 H, CH_3), 1.43 (t, J = 7 Hz, 3 H, CH_3); UV λ_{max} 384 nm (ϵ 400), 290 (4370), 228 (9470); IR (neat) 2920, 2880, 2240, 1710, 1520, 1380, 1350, 1190, 1100 cm^{-1}; MS, m/z 250 (M^+), 205, 178, 150, 122, 53 (base). Anal. Calcd for $C_{10}H_{10}N_4O_4$: C, 48.00; H, 4.03; N, 22.39. Found: C, 47.82; H, 4.02; N, 22.36.

2,9,10-Tricarbethoxy-3,8-methano-1-aza[10]annulene (6a). To a solution of **4a**[7] (2.3 g, 7.7 mmol) in ethyl acetate (15 mL) under N_2 was added benzocyclopropene (8.6 mmol) in hexane (7 mL). The solution was heated at 55 °C for 21 h and then at reflux for 5 h and evaporated. The residue was purified by chromatography (2:8 ethyl acetate/hexane) to yield 1.9 g (67%) of **6a** as a yellow solid. An analytical sample was obtained by recrystallization from methanol: mp 108.5–109.5 °C; ^{13}C NMR δ 166.06, 164.43, 163.46, 145.93, 144.18, 132.18, 131.24, 129.75, 129.62, 125.97, 124.28, 119.47, 62.42, 62.19, 34.43, 14.17, 14.01; UV λ_{max} 364 nm (ϵ 4940), 280 (17 100), 244 (24 300); IR (KBr) 2980, 1715, 1370, 1230, 1150, 1030 cm^{-1}; MS, m/z 359 (M^+, base), 314, 286, 285, 213, 140. Anal. Calcd for $C_{19}H_{21}NO_6$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.20; H, 5.92; N, 3.97.

2-Cyano-9,10-dicarbethoxy-3,8-methano-1-aza[10]annulene (6b). To a solution of **4b** (5.5 g, 22 mmol) in ethyl acetate under N_2 was added benzocyclopropene (22 mmol) in hexane (28.5 mL). The solution was heated at reflux for 17 h and then evaporated. The residue was purified by chromatography (2:8 ethyl acetate/hexane), which after recrystallization from methanol afforded 4.77 g (70%) of **6b**: mp 97–98 °C; ^{13}C NMR δ 165.28, 163.68, 149.19, 132.09, 130.88, 130.30, 129.42, 126.62, 125.91, 125.55, 120.25, 113.88, 62.71, 62.55, 33.61, 14.17, 13.95; UV λ_{max} 360 nm (ϵ 4900), 283 (18 500), 251 (19 500); IR (KBr) 2980, 2220, 1715, 1400, 1360, 1320, 1240, 1180, 1150, 1045, 1015 cm^{-1}; MS, m/z 312 (M^+), 283, 267, 239, 211, 194, 168 (base). Anal. Calcd for $C_{17}H_{16}N_2O_4$: C, 65.38; H, 5.16; N, 8.97. Found: C, 65.26; H, 5.17; N, 8.99.

9,10-Dicarbethoxy-3,8-methano-1-aza[10]annulene (6c). To a solution of **4c** (227 mg, 1 mmol) in dichloromethane (1.5 mL) was added benzocyclopropene (0.92 mmol) in hexane (0.3 mL). The solution was placed in a pressure vessel, pressured at 15 kbar and left at 55 °C for 27 h. The solution was then evaporated and the residue chromatographed (3:7 ethyl acetate/hexane) to give 109 mg (41%) of **6c** as a yellow oil. Molecular distillation (140 °C (0.1 torr)) furnished the analytical sample, which hydrated upon exposure to air prior to combustion analysis: UV λ_{max} 333 nm (ϵ 3730), 275 (12 680), 246 (15 560); IR (neat) 2970, 1710, 1600, 1460, 1370, 1225, 1100 cm^{-1}; MS, m/z 287 (M^+), 258, 242, 214, 143 (base), 141. Anal. Calcd for $C_{16}H_{17}NO_4 \cdot 1H_2O$: C, 62.94, H, 6.27; N, 4.59. Found: C, 62.85; H, 6.20; N, 4.70.

2-Carbethoxy-3,8-methano-1-aza[10]annulene (6d). To a solution of **4d** (129 mg, 0.84 mmol) in dichloromethane (1 mL) was added benzocyclopropene (0.77 mmol) in hexane (0.25 mL). The solution was placed in a pressure vessel, pressured at 15 kbar, and left at 55 °C for 27 h. The solution was then evaporated and the residue chromatographed (1:1 ethyl acetate/hexane) to give 54 mg (33%) of **6d** as a dark red oil: UV λ_{max} 377 nm (ϵ 2280), 335 (3670), 267 (14 180), 242 (17 620); IR (neat) 2970, 1710, 1450, 1290, 1270, 1170, 1090, 1040 cm^{-1}; MS, m/z 215 (M^+), 186, 169, 141 (base), 115; HRMS; calcd for $C_{13}H_{13}NO_2$ 215.09462, found 215.09457.

2-Carbomethoxy-9,10-dicarbethoxy-3,8-methano-1-aza[10]annulene (6g). A solution of **6a** (32.4 mg, 0.09 mmol) in ethanol (6 mL) was treated with KOH (5 mg, 0.09 mmol) at room temperature for 16 h. The solution was treated with Dowex 50W-X8 and evaporated, and then reacted with excess diazomethane in ether/methanol followed by an acetic acid quench. The solution was evaporated and the residue purified by preparative thin-layer chromatography (4:6 ethyl acetate/hexane) to give 19.2 mg (60%) of **6g**, which was recrystallized from methanol: mp 127–128 °C; UV λ_{max} 364 nm (ϵ 4920), 281 (17 400), 253 (24 200); IR (KBr) 2970, 1720, 1430, 1230, 1140 cm^{-1}; MS, m/z 345 (M^+), 300, 285, 272, 239, 211, 140 (base). Anal. Calcd for $C_{18}H_{19}NO_6$: C, 62.60; H, 5.55; N, 4.06. Found: C, 62.33; H, 5.61; N, 3.98.

9,10-Dicarbethoxy-2-ethoxy-3,8-methano-1-aza[10]annulene (6h). To a solution of **6b** (156 mg, 0.50 mmol) in ethanol (5 mL) was added KOH (28 mg, 0.50 mmol) in ethanol (1.2 mL). After 30 min, the solution was evaporated and the residue purified by chromatography (1:1 ethyl acetate/hexane) to give 150 mg (88%) of **6h**. Molecular distillation afforded the analytical sample: bp 145 °C (0.05 torr); ^{13}C NMR δ 167.78, 165.83, 162.45, 141,74, 128.48, 126.33, 126.27, 125.32, 121.85, 94.28, 91.94, 63.78, 61.58, 28.77, 14.24; UV λ_{max} 330 nm (ϵ 5340), 273 (15 700), 252 (18 800); IR (neat) 2970, 1720, 1470, 1370, 1220, 1130 cm^{-1}; MS, m/z 331 (M^+), 316, 303, 286, 257, 256, 242, 228 (base), 213. Anal. Calcd for $C_{18}H_{21}NO_5$: C, 65.24; H, 6.39; N, 4.23. Found: C, 65.13; H, 6.43; N, 4.14.

9-Carbethoxy-10-carboxy-2-cyano-3,8-methano-1-aza[10]annulene (6i). A solution of **6b** (335 mg, 1.07 mmol) in tetrahydrofuran (8 mL) was treated with KOH (75 mg, 1.3 mmol) in water (9 mL) for 2 h. The solution was partitioned between ether and water. The aqueous phase was acidified with HCl and then extracted into ether. The ether extract was dried over Na_2SO_4 and evaporated to give 319 mg (100%) of pure **6i**, which was recrystallized from methanol/water: mp 147–151 °C; ^{13}C NMR δ 163.62, 163.42, 143.63, 132.54, 131.63, 131.31, 130.33, 129.62, 126.46, 124.61, 121.03, 113.56, 63.23, 33.09, 13.75; UV λ_{max} 358 nm (ϵ 5130), 273 (20 300), 257 (20 800); IR (KBr) 3300, 2970, 2230, 1760, 1710, 1400, 1330, 1230 cm^{-1}; MS, m/z 284 (M^+), 256, 238,

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(14) Schmidt, P.; Druey, J. *Helv. Chim. Acta* **1955**, *38*, 1560.

211, 194, 168, 166 (base). Anal. Calcd for $C_{15}H_{12}N_2O_4$: C, 63.38; H, 4.25; N, 9.85. Found: C, 63.17; H, 4.29; N, 9.80.

9-Carbethoxy-2-cyano-3,8-methano-1-aza[10]annulene (6j). A solution of **6i** (122 mg, 0.43 mmol) in xylene (8 mL) was heated at reflux for 40 min. The solution was diluted with ether, washed with saturated $NaHCO_3$ and then brine, dried over Na_2SO_4, and evaporated. The residue was chromatographed (2:8 ethyl acetate/hexane) to give 59 mg (57%) of **6j**. Molecular distillation afforded the analytical sample: bp 140 °C (0.1 torr); ^{13}C NMR δ 164.24, 150.10, 132.67, 131.40, 130.72, 129.36, 128.57, 123.60, 119.00, 118.46, 114.76, 61.90, 33.68, 14.34; UV λ_{max} 397 nm (ε 3390), 354 (4360), 282 (20 400), 245 (20 800); IR (neat) 2970, 2220, 1710, 1500, 1290, 1230, 1100, 1060 cm^{-1}; MS, *m/z* 240 (M^+), 212, 211, 195, 167, 140 (base). Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.73; H, 5.05; N, 11.42.

9,10-Dicarbethoxy-1,2-dihydro-2-hydroxy-3,8-methano-1-aza[10]annulene (7). Preparative thin-layer chromatographic purification (3:7 ethyl acetate/hexane) of **6c** (28 mg) afforded 6 mg of **7**, which was isolated as a yellow crystalline solid: mp 107–109 °C; MS, *m/z* 305 (M^+), 259, 230 (base). For a combustion analysis see the preparation of **6c**. Alternatively, a solution of **6a** (44.8 mg, 0.13 mmol) in ethanol (5 mL) was treated with KOH (8.1 mg, 0.14 mmol) at room temperature for 16 h and then evaporated. To the residue in dry THF (5 mL) at 0 °C was added oxalyl chloride (120 μL, 1.4 mmol). After 1 h the solution was evaporated, the residue was dissolved in THF (3 mL) and the resulting solution was cooled to 0 °C. A solution of *tert*-butyl hydroperoxide (93 mg, 1 mmol) in pyridine (1 mL) was added. After 1 h, the solution was taken up in ether, washed with water and then brine, dried over Na_2SO_4, and evaporated to give a yellow oil weighing 20 mg. This oil was dissolved in toluene (5 mL), and the solution was heated at reflux for 30 min and then evaporated. Preparative thin-layer chromatography (3:7 ethyl acetate/hexane) afforded 2.4 mg (7%) of hydrate **7**.

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Registry No. **3**, 4646-69-9; **4a**, 74476-38-3; **4b**, 74476-39-4; **4c**, 74476-40-7; **4d**, 6498-02-8; **6a**, 74476-41-8; **6b**, 74476-42-9; **6c**, 74476-43-0; **6d**, 74476-44-1; **6e**, 88729-98-0; **6g**, 88729-99-1; **6h**, 88730-00-1; **6i**, 88746-41-2; **6j**, 88730-01-2; **7**, 88730-02-3; diethyl dioxosuccinate, 59743-08-7; cyanoformamidrazone, 54606-55-2.

Chemistry of Bis(alkoxycarbonyl)polysulfanes and Related Compounds[1]

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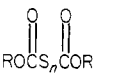
Bis(alkoxycarbonyl)polysulfanes **3–6** with up to six sulfurs have been prepared by reaction of dichlorosulfanes with 2 equiv of *O,O'*-dialkyl thiocarbonates (**16**). This method is compared to several literature methods for the preparation of **1–6** together with some new methods, including the hydrolysis of bis(alkoxydichloromethyl)-polysulfanes **18–21** in turn derived from the chlorination of bis(alkoxythiocarbonyl)polysulfanes. Related chemistry provided (methoxycarbonyl)disulfanyl chloride (**15a**), (methoxydichloromethyl)disulfanyl chloride (**24a**), (chlorocarbonyl)disulfanyl chloride (**26**), and bis(chlorocarbonyl)trisulfane (**29**), all in good yields. Bis(alkoxycarbonyl)polysulfanes **1–9** with up to nine sulfurs were isolated from the alcoholysis of (alkoxycarbonyl)(alkoxydichloromethyl)di- and -trisulfanes **30, 31**, and **35** and (alkoxydichloromethyl)(chlorocarbonyl)polysulfanes **39–41**. The higher sulfanes **7–9** were identified by their HPLC behavior where a plot of log (retention time) against the number of sulfurs was found to be linear. Mechanisms for the formation of these products are proposed.

As part of the development of a general set of methods for the synthesis of bis(chlorocarbonyl)disulfane (**10**) and related compounds with a dithiocarbonyl function, we reported[3] the preparation of bis(alkoxycarbonyl)disulfanes (**2**); in a different context,[4] we observed bis(alkoxycarbonyl)trisulfanes (**3**). Ongoing studies[3,5] provided a variety of (alkoxydichloromethyl)sulfanes that have now been subjected to alcoholysis and shown to provide a series of bis(alkoxycarbonyl)polysulfanes **2–9**. Interest in this



1, *n* = 1 **4**, *n* = 4 **7**, *n* = 7
2, *n* = 2 **5**, *n* = 5 **8**, *n* = 8
3, *n* = 3 **6**, *n* = 6 **9**, *n* = 9

a, R = CH_3 b, R = C_2H_5

class of compounds led us to further investigate methods for their preparation. The products made according to prior literature methods, many of which date back more than 50 years, have been quantitatively analyzed by HPLC and compared to products made by several new techniques which are reported here. HPLC revealed the proportions of the different bis(alkoxycarbonyl)polysulfanes in the reaction mixtures, and the linearity of a plot of log (retention time) vs. number of sulfurs was taken as good evidence for the identity of the higher members of the homologous series.

Table I shows the structural formulas together with ^1H and ^{13}C NMR data for the compounds discussed in this

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(2) Searle Scholar, 1982; National Institutes of Health Research Career Development Award, AM 01099, 1982–1987.

(3) Barany, G.; Schroll, A. L.; Mott, A. W.; Halsrud, D. A. *J. Org. Chem.* **1983**, *48*, 4750–4761. This manuscript contains many of the general procedures of organosulfur chemistry as practiced in this laboratory, together with details on the preparations of several key starting materials.

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