Anal. Calcd for $C_{16}H_{16}O_4S$: C, 63.14; H, 5.30; S, 10.54. Found: C, 62.84; H, 5.05; S, 10.47.

1-(2-Methylsulfonylbenzoyl)pyrrolidine (19).—A combination of 6.4 g (0.035 mol) of **1**, 100 ml of benzene, and 10 g (0.141 mol) of pyrrolidine was refluxed overnight in a Dean–Stark apparatus for removal of water. After evaporating to dryness, recrystallization from chloroform–hexane gave 1.2 g (14%) of product: mp 113–115°; ir, 6.15 (C=O), 7.65 and 8.70 μ (SO_2); nmr ($DCCl_3$), τ 8.05 (m, 4), 6.71 (s, 3, CH_3), 6.4 and 6.8 (m, 4), 2.2 (m, 4, aromatic protons).

Anal. Calcd for $C_{12}H_{15}NO_3S$: C, 56.89; H, 5.97; N, 5.53. Found: C, 56.59; H, 5.90; N, 5.52.

The Enamine from 1 and Pyrrolidine (18).—Repetition of the experiment used for **19**, except that only 2 equiv of pyrrolidine was employed, produced after evaporation and recrystallization from chloroform–hexane 0.84 g (11%) of the enamine **18**: mp 219–220° dec; uv max (EtOH), 252 mμ (ϵ 12,050), 348 (2900); nmr ($DCCl_3$), τ 8.0 (m, 4), 6.4 (m, 4), 4.86 (s, 1, the 2 proton), 2.4 (m, 4).

Anal. Calcd for $C_{12}H_{13}NO_2S$: C, 61.25; H, 5.57; N, 5.95. Found: C, 61.05; H, 5.50; N, 5.87.

Bis(3-hydroxybenzo[*b*]thien-2-yl 1,1-dioxide)methane (20).—To a suspension of 1.7 g (0.035 mol) of 50% sodium hydride in oil in 35 ml of dry N,N-dimethylformamide was added a solution of 6.4 g (0.035 mol) of **1** in 20 ml of N,N-dimethylformamide. When vigorous gas evolution had subsided, a solution of 3.4 g (0.035 mol) of chloromethyl methyl sulfide in 10 ml of dimethylformamide was added. After stirring 2 hr while a fine white solid precipitated, the solution was poured into 250 ml of water and was acidified with 3 *N* HCl which yielded a soft solid. Trituration with hot ethanol gave, in two crops, 3.0 g (46%) of **20**: mp 254–255°; ir, 5.75 (C=O), 7.60, and 8.71 μ (SO_2); nmr (DMSO-d_6), τ 1.9 (m, 4), 5.1 (t, 2, J = 8 cps, exchanges with D_2O, the 2 proton), 7.15 (d, 2, J = 8 cps, CH_2). A sample of **20** was found to be insoluble in H_2O but dissolved to a yellow solution in warm, dilute NaOH.

Anal. Calcd for $C_{17}H_{12}O_6S_2$: C, 54.24; H, 3.21; S, 17.01. Found: C, 54.11; H, 3.39; S, 16.92.

Registry No.—**1**, 1127-35-1; **2**, 17288-99-2; **3**, 17289-00-8; **4**, 17289-01-9; **5**, 17289-02-0; **6**, 17289-03-1; **7**, 17289-04-2; **8**, 17289-05-3; **9**, 17289-06-4; **11**, 17289-07-5; **12**, 17289-08-6; **13**, 17289-09-7; **14**, 17289-10-0; **15**, 17289-11-1; **16**, 17289-12-2; **17**, 17322-89-3; **18**, 17289-13-3; **19**, 17289-14-4; **20**, 17289-15-5.

Acknowledgment.—The author is grateful to Mr. Nelson Treadway, Jr., for his capable assistance in the synthetic work.

Heterocycles from Hydrazino Alcohols. An Unusual Carbon–Carbon Bond Cleavage

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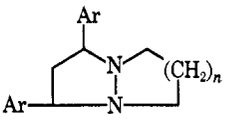
Received May 9, 1968

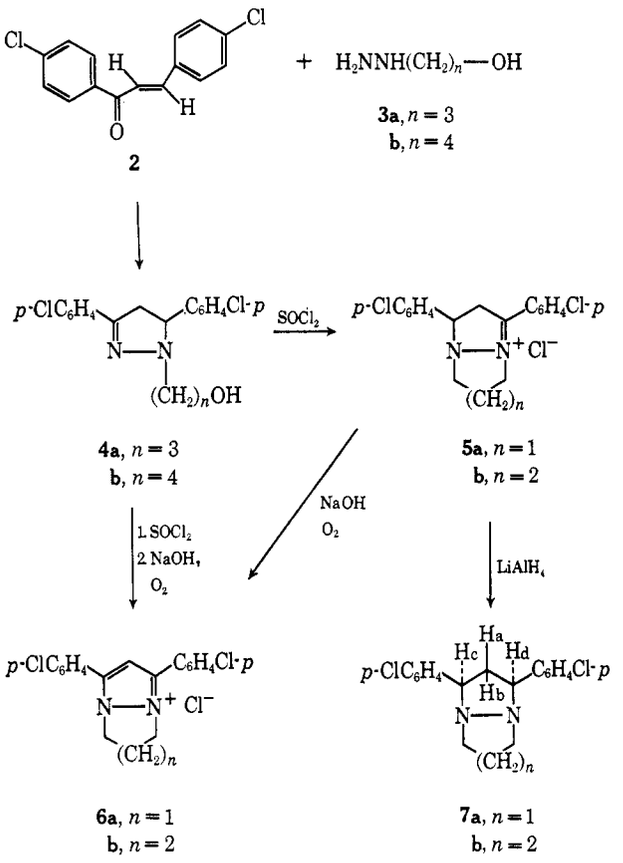
As part of a program directed to the synthesis of bridgehead hydrazine heterocycles with potential medicinal interest, we wished to prepare 1,3-diaryl derivatives of perhydropyrazolo[1,2-*a*]pyrazole (**1a**) and pyridazo[1,2-*a*]pyrazole (**1b**). Since the present synthetic routes[2] for preparing these ring systems do not afford easy access to 1,3-diaryl derivatives, we have investigated the possibility of preparing them from hydrazino alcohols and chalcones. In this note we wish to report the preparation of **1a** from these intermediates and an unusual lithium aluminum hydride cleavage of a carbon–carbon bond during the attempted preparation of **1b**.



1a, $n = 1$
b, $n = 2$

The treatment of 4,4′-dichlorochalcone (**2**) with 3-hydrazinopropanol (**3a**) in refluxing benzene (Scheme I) resulted in the formation of 3,5-bis-*p*-chlorophenyl-

SCHEME I



2 + $H_2NNH(CH_2)_n$—OH (**3a**, $n = 3$; **b**, $n = 4$)

4a, $n = 3$; **b**, $n = 4$ — $SOCl_2$ → **5a**, $n = 1$; **b**, $n = 2$

4a, **b** → 1. $SOCl_2$ 2. NaOH, O_2 → **6a**, $n = 1$; **b**, $n = 2$

4a, **b** → NaOH, O_2 → **6a**, $n = 1$; **b**, $n = 2$

5a, **b** → $LiAlH_4$ → **7a**, $n = 1$; **b**, $n = 2$

1-(3-hydroxypropyl)-4,5-dihydropyrazole (**4a**). Treatment of **4a** with thionyl chloride in chloroform followed by *in vacuo* removal of the excess reagent gave 5,7-bis-(*p*-chlorophenyl)-2,3,6,7-tetrahydro-1H-pyrazolo[1,2-*a*]pyrazol-4-ium chloride (**5a**). If the reaction of **4a** with thionyl chloride was processed with aqueous sodium hydroxide, there was obtained **5a** and 5,7-bis-(*p*-chlorophenyl)-2,3-dihydro-1H-pyrazolo[1,2-*a*]pyrazol-4-ium chloride (**6**). Compound **6** could also be obtained by treating **5a** with aqueous sodium hydroxide in the presence of air. This transformation probably occurs by base-catalyzed air oxidation at C-3 in **5a** followed by loss of water or hydrogen peroxide. Similar oxidative dehydrogenations have been reported with simple pyrazole[3] derivatives. Treatment of **5a**

(1) (a) To whom inquiries should be addressed. (b) Celanese Research Co., Summit, N. J.

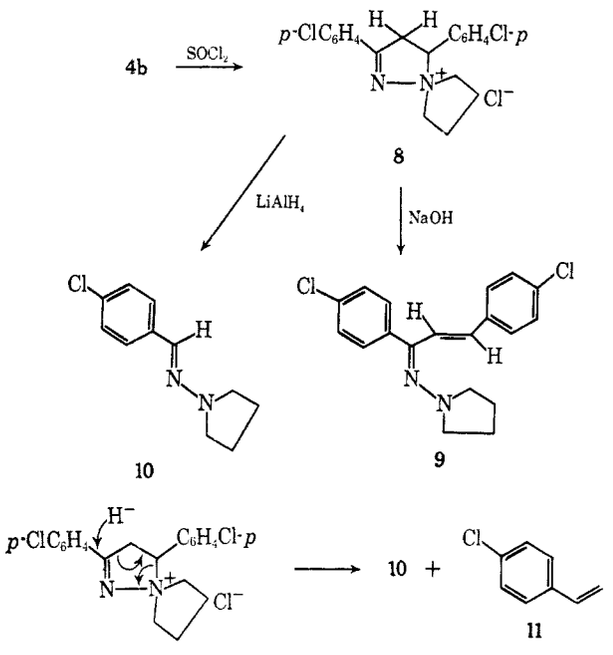
(2) W. A. Mosby, "Heterocyclic Systems with Bridgehead Nitrogen Atoms," Interscience Publishers, New York, N. Y., 1961, Chapter III, pp 215–224; part 2, Chapter XIV, pp 1241–1242; T. W. G. Solomons and C. F. Voight, *J. Amer. Chem. Soc.*, **88**, 5588 (1966); S. Arofimenko, *ibid.*, **87**, 4394 (1965); H. Stetter and K Findeisen, *Chem. Ber.*, **98**, 3228 (1965).

(3) T. L. Jacobs in "Heterocyclic Compounds," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1957, pp 108–110.

with excess lithium aluminum hydride resulted in the reduction of the immonium group to give **7a**. The *cis* configuration was indicated for **7a** by nmr which showed H_a and H_b having chemical shifts separated by about 0.9 ppm, whereas, if the compound were in the *trans* configuration, protons H_a and H_b would be expected to be equivalent.

With the expectation that **7b** could be obtained from a similar synthetic sequence, **4b** was prepared from 4-hydrazinobutanol (**3b**) and 4,4′-dichlorochalcone (**2**). After **4b** was refluxed with thionyl chloride a quaternary salt was isolated (Scheme II). That this substance was the spiro system **8** rather than the desired **5b** was indicated when treatment with aqueous sodium hydroxide did not give the expected aromatic system **6b**. Instead, a β-elimination (Hofmann type) occurred in **8** to give the Schiff base **9**. The reduction of **8** with lithium aluminum hydride gave 4-chloro-N-pyrrolidylbenzaldimine (**10**) as the only isolable product. This unusual cleavage could result from a hydride attack on the imine carbon of **8** followed by bond reorganization to give **10** and *p*-chlorostyrene (**11**). Several unsuccessful attempts were made to isolate **11**.

SCHEME II



Experimental Section[4]

3,5-Bis(*p*-chlorophenyl)-1-(3-hydroxypropyl)-4,5-dihydropyrazole (4a).—A mixture of 50 g (0.18 mol) of 4,4′-dichlorochalcone,[5] 16.4 g (0.18 mol) of 3-hydrazinopropanol,[6] and 1000 ml of benzene was stirred and refluxed in a flask equipped with a Dean–Stark tube until the water layer in the tube remained constant. The solvent was removed *in vacuo* and the residue was taken up in anhydrous tetrahydrofuran and treated with anhydrous hydrogen chloride to give 36.8 g of **4a** hydrochloride: mp 177–181° (methanol–ether); ir (KBr), 3.05, 6.21, 6.28 μ; uv, λ_{max}^{EtOH} 225 mμ (ε 19,750), 312 (14,360). The free base gave nmr ($CDCl_3$) signals at δ 1.68 (2 H, m, C—CH_2—C), 2.69 (1 H, D_2O exchangeable, OH), 2.92 (4 H, m, CH_2N and CH_2C=), 3.58 (2 H, t, J = 7 cps, CH_2OH), 4.22 (1 H, m, ArCH), 7.36 (8 H, m, Ar).

Anal. Calcd for $C_{18}H_{19}Cl_3N_2O$: C, 56.0; H, 5.0; Cl, 27.6; N, 7.3. Found: C, 56.1; H, 5.0; Cl, 27.1; N, 7.3.

3,5-Bis(*p*-chlorophenyl)-1-(4-hydroxybutyl)-4,5-dihydropyrazole (4b).—Following the procedure used to prepare **4a** a mixture of 30.0 g (0.11 mol) of 4,4′-dichlorochalcone, 11.3 g (0.11 mol) of 4-hydrazinobutanol,[6] and 500 ml of benzene gave 40.8 g of **4b** as a yellow oil. Distillation of a 1.0-g sample of **4b** in a kugelrohr gave 0.90 g of **4b** at 185° (0.20 mm): uv, λ_{max}^{EtOH} 223 mμ (ε 19,500), 311 (14,250); nmr ($CDCl_3$), δ 1.67 (4 H, m, >CCH_2CH_2C<), 2.65 (1 H, D_2O exchangeable, OH), 2.83 (4 H, m, CH_2N and CH_2C=), 3.54 (2 H, t, J = 6.0 cps, CH_2OH), 4.20 (1 H, q, J = 9.5 cps, ArCH), 7.34 (8 H, m, Ar).

Anal. Calcd for $C_{19}H_{20}Cl_2N_2O$: C, 62.8; H, 5.5; Cl, 19.6; N, 7.7. Found: C, 62.8; H, 5.7; Cl, 19.4.

5,7-Bis(*p*-chlorophenyl)-2,3,6,7-tetrahydro-1H-pyrazolo[1,2-*a*]pyrazol-4-ium Chloride (5a).—A solution of 31.7 g (0.09 mol) of **4a**, 16.0 g (0.14 mol) of thionyl chloride, and 320 ml of chloroform was stirred and refluxed for 20 hr. The solvent was removed *in vacuo* and the residue was crystallized from ethanol–diethyl ether to give 12.0 g (36%) of **5a**: mp 189–190°; ir ($CHCl_3$), 3.42, 4.08 (C=N—N^+), 6.28, 9.16, 9.88 μ; uv, λ_{max}^{EtOH} 264 mμ (ε 10,980), 320 (13,615); nmr ($CDCl_3$–d_6-DMSO), δ 2.51–4.10 (6 H, m) 4.38–5.68 (3 H, m), 7.20–8.18 (8 H, m, Ar).

Anal. Calcd for $C_{18}H_{17}Cl_3N_2$: C, 58.7; H, 4.6; Cl, 29.1. Found: C, 58.4; H, 4.8; Cl, 28.9.

5,7-Bis(*p*-chlorophenyl)-2,3-dihydro-1H-pyrazolo[1,2-*a*]pyrazol-4-ium Chloride (6a).—A mixture of 1.0 g of **5a** and 20 ml of 2 *N* sodium hydroxide was stirred at room temperature for about 20 hr. The resultant solid was filtered off and crystallized from ethanol–diethyl ether to give 0.500 g (52%) of **6a**: mp 256–259°; ir (KBr), 2.91, 6.22, 6.74, 9.16, and 9.90 μ; uv, λ_{max}^{EtOH} 245 mμ sh (ε 22,200), 274 (27,530); nmr (CF_3COOH), δ 3.22 (2 H, m, >C–CH_2–C<), 4.81 (4 H, m, CH_2NNCH_2), 7.10 (1 H, s, HC=), 7.34 (8 H, m, $C_{12}H_8Cl_2$).

Anal. Calcd for $C_{18}H_{15}Cl_3N_2$: C, 58.9; H, 4.4; Cl, 29.1; N, 7.6. Found: C, 58.6; H, 4.2; Cl, 28.8; N, 7.6.

Compound **6a** was also obtained in the preparation of **5a** when the excess thionyl chloride was decomposed with 2 *N* sodium hydroxide.

A solution of 0.200 g of **6a** in 2.0 ml of ethanol treated with 0.20 ml of 70% perchloric acid gave an immediate precipitate of 0.210 g of **6a** perchlorate, mp 283–284.5°.

Anal. Calcd for $C_{18}H_{15}Cl_3N_2O_4$: C, 50.3; H, 3.5; Cl, 24.7; N, 6.5. Found: C, 50.6; H, 3.6; Cl, 25.0; N, 6.4.

1,3-Bis(*p*-chlorophenyl)-2,3,6,7-tetrahydro-1H,5H-pyrazolo[1,2-*a*]pyrazole (7a).—A mixture of 13.9 g (0.04 mol) of **5a**, 3.2 g (0.08 mol) of lithium aluminum hydride, and 400 ml of absolute tetrahydrofuran was stirred and refluxed for about 20 hr under a nitrogen atmosphere. The reaction was cooled in an ice bath and treated successively with 6.4 ml of 2 *N* sodium hydroxide, 9.6 ml of water, and then anhydrous sodium sulfate. The salts were filtered off and the filtrate was concentrated *in vacuo* to give 11.4 g of a yellow oil that crystallized from isopropyl alcohol. Vacuum sublimation (0.5 mm, 50°) of this material gave 6.5 g (49%) of **7a**: mp 75–77°; nmr ($CDCl_3$), δ 2.05 (3 H, m, C-6H_2 and H_a), 2.96 (5 H, m, CH_2NNCH_2 and H_b), 4.03 (3 H, m, H_c and H_d), 7.80 (8 H, m, $C_{12}H_8Cl_2$).

Anal. Calcd for $C_{18}H_{18}Cl_2N_2$: C, 6.49; H, 5.4; N, 8.4. Found: C, 65.2; H, 5.6; N, 8.2.

A solution of 0.200 g of **7a**, 2.5 ml of methyl iodide, and 5.0 ml of anhydrous tetrahydrofuran was stirred for 24 hr at room temperature to give 0.275 g of **7a** methiodide, mp 225–226°.

Anal. Calcd for $C_{19}H_{21}Cl_2IN_2$: C, 48.0; H, 4.5; I, 26.7; N, 6.2. Found: C, 48.1; H, 4.5; I, 27.0; N, 6.0.

2,4-Bis(*p*-chlorophenyl)-1-aza-5-azaniaspiro[4.4]non-1-ene Chloride (8).—A mixture of 22.8 g (0.06 mol) of **4b**, 11.1 g (0.09 mol) of thionyl chloride, and 230 ml of chloroform was stirred and refluxed for 18 hr. The reaction mixture was allowed to cool to room temperature and then extracted twice with 2 *N* sodium hydroxide and saturated sodium chloride solution. The chloroform layer was dried (Na_2SO_4), filtered, and concentrated *in vacuo* to give 24.7 g of oil that solidified when treated with diethyl ether. Crystallization from tetrahydrofuran gave 15.0 g of **8**: mp 163–165° dec; ir (KBr), 2.98, 6.21, 6.30, and 9.20

(4) Melting points were determined on a Thomas–Hoover capillary melting point apparatus and have not been corrected. Proton nmr spectra were obtained in a Varian Associates A-60 spectrometer and are recorded in parts per million (δ) from an internal Me_4Si standard. Infrared spectra were determined using a Perkin-Elmer Infracord. Ultraviolet spectrum were obtained on a Cary Model 15 spectrophotometer.

(5) F. Strauss and A. Ackermann, *Ber.*, **42**, 1804 (1909).

(6) G. Gever, *J. Amer. Chem. Soc.*, **76**, 1283 (1954).

μ; uv, λ_{max}^{EtOH} 264 mμ (ϵ 21,415); nmr ($CDCl_3$), δ 2.20 (4 H, m, CCH_2CH_2C), 3.52 (4 H, m, $CH_2N^+CH_2$), 4.39 (2 H, m, $N{=}CCH_2$), 6.52 (1 H, m, CHAr), 7.68 (8 H, m, $C_{12}H_8Cl_2$).

Anal. Calcd for $C_{19}H_{19}Cl_3N_2$: C, 59.8; H, 5.0; Cl, 27.9; N, 7.3. Found: C, 59.6; H, 5.2; Cl, 26.9; N, 7.1.

A solution of **8** in ethanol treated with excess 70% perchloric acid gave an immediate precipitate of **8** perchlorate, mp 249.5–250°.

Anal. Calcd for $C_{19}H_{19}Cl_3N_2O_4$: C, 51.2; H, 4.3; Cl, 23.9; O, 14.4. Found: C, 51.3; H, 4.4; Cl, 23.8; O, 14.3.

Sodium Hydroxide Conversion of 8 into 9.—A mixture of 1.0 g of **8** and 50 ml of 2 *N* sodium hydroxide was stirred for 3 hr at room temperature. The oil that separated during this time was extracted with chloroform, dried (Na_2SO_4), filtered, and concentrated *in vacuo* to give 0.900 g of an oil that solidified on standing. Crystallization from ethanol–water gave 0.539 g of yellow **9**: mp 96–96.5°; ir (KBr), 6.72, 9.21, and 9.93 μ; uv, λ_{max}^{EtOH} 280 mμ (ϵ 25,000), 373 (7500); nmr ($CDCl_3$), δ 1.86 (4 H, m, CCH_2CH_2C), 3.29 (4 H, m, CH_2NCH_2), 6.90 (2 H, AB, J = 17 cps, $HC{=}CH$), 7.38 (8 H, m, $C_{12}H_8Cl_2$).

Anal. Calcd for $C_{19}H_{18}Cl_2N_2$: C, 66.1; H, 5.3; Cl, 20.5. Found: C, 66.3; H, 5.3; Cl, 20.5.

Lithium Aluminum Hydride Reduction of 8 to 10.—To a stirred slurry of 0.99 g (0.026 mol) of lithium aluminum hydride in 45 ml of anhydrous tetrahydrofuran maintained under a nitrogen atmosphere there was added in one portion 5.0 g (0.013 mol) of **8**. The mixture was refluxed for 18 hr, cooled in an ice bath, and treated successively with 5.0 ml of ethyl acetate, 2.0 ml of 2 *N* sodium hydroxide, 3.0 ml of water, and 5 g of anhydrous sodium sulfate. The salts were filtered off and the filtrate was concentrated *in vacuo* to give an oil that crystallized from ligroin. Recrystallization from methanol gave 0.64 g (24%) of **10**: mp 90–91.5°; ir ($CHCl_3$), 6.33, 6.48 and 6.76 μ; uv, λ_{max}^{EtOH} 230 mμ (ϵ 8100), 314 (22,000); nmr ($CDCl_3$), δ 1.91 (4 H, m, CCH_2CH_2C), 3.31 (4 H, m, CH_2NCH_2), 7.05 (1 H, s, $ArCH{=}$), 7.35 (4 H, A_2B_2,C_6H_4).

Anal. Calcd for $C_{11}H_{13}ClN_2$: C, 63.3; H, 6.2; Cl, 17.0; N, 13.4. Found: C, 63.6; H, 6.5; Cl, 17.1; N, 13.4.

A solution of 0.605 g (0.0043 mol) of *p*-chlorobenzaldehyde and 0.371 g (0.0043 mol) of N-aminopyrrolidine in 1.0 ml of ethanol was warmed on a water bath for about 5 min and then cooled in an ice bath. The resultant solid was filtered off and crystallized from ethanol to give 0.714 g of **10**, mp 91–92°. Comparison of the infrared spectrum and the mixture melting of **10** prepared from **8** showed them to be identical.

Registry No.—**4a**, 17288-70-9; **4a**·HCl, 17288-66-3; **4b**, 17288-71-0; **5a**, 17288-72-1; **6a**, 17288-73-2; **6a** perchlorate, 17288-74-3; **7a**, 17288-75-4; **7a** methiodide, 17326-50-0; **8**, 17288-76-5; **8** perchlorate, 17288-77-6; **9**, 17288-79-8; **10**, 17288-78-7.

Acknowledgment.—The authors thank Mr. Paul Schirm for assistance in the synthetic work and Mr. Urs Stoeckli for analytical and instrumental analyses.

Bromination of 1,2-Cyclononadiene. Preparation of *cis*- and *trans*-2,3-Dibromocyclononene[1]

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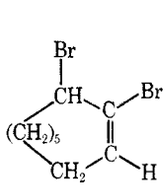
Received January 10, 1968

Halogen additions to only a relatively few allenes have been reported.[2] In no case where geometrical isomerism of the carbon–carbon double bond of the monoaddition product was possible has the stereochemistry been determined.[3]

The reaction of 1 mol of bromine with 1,2-cyclononadiene in carbon tetrachloride has been investigated and shown to yield a mixture of *cis*- and *trans*-2,3-dibromocyclononene (**1** and **2**, respectively). The twice-distilled material (about 30% yield) was shown by gas chromatography (Carbowax 20M liquid phase) to consist of 85% of **1** and **2**. Treatment of this material with either aqueous or ethanolic silver nitrate immediately gave a precipitate, indicating the presence of an allylic bromine atom. The presence of a carbon–carbon double bond was indicated by a medium intensity ir absorption at 1635 cm^{-1}. When the twice distilled material was debrominated with either zinc or magnesium, 1,2-cyclononadiene was the sole product detected by gas chromatography, and both of the major peaks of the starting material had completely disappeared.



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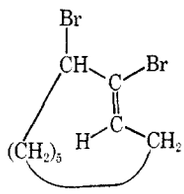

2

A sample of **1** and **2** purified by gas chromatography (the sample consisted of the two major components which had retention times of 28.0 and 30.5 min on a Carbowax 20M column at 152°) gives the following nmr spectrum: two overlapping triplets centered at τ 3.89 (J = 8.8 cps) and 4.11 (J = 8.8 cps) with a total relative area of 1.0 correspond to a vinyl proton split by adjacent methylene protons in each of the two isomers (**1** and **2**); a quartet at 4.86 (J = 5.3 cps) and a quintet at 5.84 (J = 5.8 cps) with a total relative area of 1.0 correspond to the methine protons of the two isomers;[4,5] a complex absorption between 7.05 and 8.90 with a total relative area of 12.0 corresponds to the 12 methylene protons.

An attempt was made to isolate **1** and **2** by preparative gas chromatography using a Carbowax 20M column. Because the 30.5-min peak tailed into the 28.0-min peak, it was not possible to collect a sample significantly enriched in the 28.0-min retention time component. The separation of the component with the 30.5-min retention time was accomplished, however. Its nmr spectrum revealed a triplet (J = 8.8 cps) at τ 4.11 (relative area = 1.0), a quintet (J = 5.8 cps) at 5.84 (relative area = 1.0), and a complex multiplet between 7.05 and 8.90 (relative area = 12.0). The peaks at τ 3.89 and 4.86 as well as part of the com-

(1) From the Ph.D. Thesis of M. J. Millam, University of the Pacific, 1966.

(2) S. Patai, "The Chemistry of Alkenes," John Wiley and Sons, Inc., New York, N. Y., 1964, p 1074 ff.

(3) The stereochemistry of the double bond of the monobromination product of 2,3-pentadiene has recently been reported, however: W. L. Waters and M. J. Caserio, Abstracts, the 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 1968, No. P43.

(4) A simple first-order analysis predicts that the two nonequivalent methylene protons[5] adjacent to the asymmetric carbon will split the methine proton into a quartet. The quartet observed at τ 4.86 accounts for the methine proton of one isomer. The methine proton at τ 5.84 has a more complex splitting than that simply predicted.

(5) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959; G. M. Whitesides, D. Holtz, and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 2628 (1964), and references therein.