was filtered and acidified to give a solid which was crystallized twice from benzene to yield pure III (1.15 g) as colorless blades, mp 218–220°.

Anal. Calcd for $C_{26}H_{18}O_4$: C, 79.17; H, 4.60. Found: C, 78.81; H, 4.70.

When the filtered, hot, alkaline solution was allowed to cool slowly to room temperature, a sodium salt separated, from which pure III could be obtained on acidification. Product III is readily soluble in 5% sodium carbonate.

Treatment of III with Hydriodic Acid and Red Phosphorus.[6]—A mixture of III (1.15 g), red phosphorus (0.6 g), 55% hydriodic acid (6 ml), and xylene (10 ml) was refluxed for 140 hr. The cooled reaction mixture was then filtered and the residue was washed with benzene and extracted with hot 2 *N* sodium hydroxide. The filtered, alkaline solution, on acidification, afforded the dicarboxylic acid IV (0.7 g). An analytical sample of the product (from acetic acid) had mp 274–276°.

Anal. Calcd for $C_{26}H_{20}O_4$: C, 78.77; H, 5.09. Found: C, 78.51; H, 5.02.

The organic combined layers were washed with 2 *N* sodium hydroxide and evaporated. Crystallization of the residue from benzene–hexane afforded V as yellow needles (80 mg): mp 220–222°; main infrared bands at 6.60, 6.70, 10.41, 10.56, 11.15, 11.35, 12.29, 12.51, 13.49, 14.30 μ; λ_{max} 216, 222, 239, 256, 284, 308, 322, 351, 410, 422 mμ (log ϵ 4.49, 4.49, 4.85, 4.66, 4.37, 4.78, 4.99, 4.50, 2.70, 2.70) (the spectrum of pentaphene[4] has maxima at 245, 257, 289, 302, 314, 329, 345, 356, 379, 399, 412, 423 mμ). The product dissolves in hot, concentrated sulfuric acid giving a pink solution with blue fluorescence. The mass spectrum of this hydrocarbon exhibits an intense molecular peak at *m/e* 328, as expected for $C_{26}H_{16}$. Also the doubly charged molecular ion is very abundant, while fragment peaks are very low.

Anal. Calcd for $C_{26}H_{16}$: C, 95.09; H, 4.91. Found: C, 94.84; H, 5.16.

Acknowledgments.—This paper is dedicated to Professor Remo de Fazi on his 75th birthday. Thanks are due to Dr. A. Mandelbaum (Technion, Israel Institute of Technology, Haifa) for the mass spectrum, Dr. V. Malaguzzi for the ultraviolet spectrum, and Professor G. Berti for full discussion of these results.

The Meisenheimer Reaction in the 1,5-Naphthyridine Series

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Meisenheimer[1] observed the formation of 4-chloroquinoline when quinoline 1-oxide was refluxed with sulfuryl chloride. Bobranski and co-workers[2] found that pyridine 1-oxide with the same reagent gave a mixture of 2- and 4-chloropyridines. Bobranski[3] showed that both 2- and 4-chloroquinolines are obtained from quinoline 1-oxide and isomers have been found in this reaction by other workers[4,5] in the pyridine series. Since Hart[6] reported the formation of only 2-chloro-1,5-naphthyridine from the action of phosphorus oxychloride on 1,5-naphthyridine 1-oxide, it was of interest to inquire whether this reaction afforded both 2-chloro and 4-chloro as expected. We have now repeated his work and wish to report that 2-chloro- and 4-chloro-1,5-naphthyridines are obtained in roughly equal amounts in this reaction. Gas chromatography confirms the presence of the two compounds. They were separated on a preparative gas chromatograph and comparison with synthetic 2- and 4-chloronaphthyridine using infrared analyses, gas chromatography retention time, and mixture melting points confirms their structures.

Experimental Section

Meisenheimer Reaction.—1,5-Naphthyridine[7] (4.5 g) was oxidized by heating to 70° with a mixture of acetic acid (10 ml) and 40% peracetic acid (5 ml) for 3 hr. The mono- and dioxides were separated by fractional crystallization using methylcyclohexane.[6] The mono-1-oxide (0.77 g) was heated to reflux with phosphorus oxychloride (30 ml) and phosphorus pentachloride for 20 min and the crude mixture was collected. This crude mixture was analyzed on a Beckman G.C. 4 gas chromatograph using a 12-ft aluminum column 0.25 in. in diameter filled with 15% SE-30 on Chromosorb W. The column temperature was 240° and the helium pressure was 40 psi. Two distinct peaks were obtained with retention times of 8.06 and 8.95 min which were subsequently identified as the 2- and 4-chloro-1,5-naphthyridines, respectively. The areas under the two curves assuming equal thermal conductivity indicate 56.8% 2-chloro-1,5-naphthyridine and 43.2% 4-chloro-1,5-naphthyridine.

2-Chloro-1,5-naphthyridine.—2-Hydroxy-1,5-naphthyridine[8] (4.9 g) was refluxed with a mixture of 5 g of phosphorus pentachloride and 100 ml of phosphorus oxychloride for 4 hr. Excess phosphorus oxychloride was removed *in vacuo*, the residue was dissolved in cold water and basified with concentrated ammonium hydroxide, and the precipitate was filtered. There was obtained 4.1 g (70% of the theoretical amount) which was recrystallized from ligroin and melted 114–116° (lit.[6] mp 112°).

4-Chloro-1,5-naphthyridine.—This compound was prepared by the method of Hauser and co-workers[9] and melted at 102–103° (lit.[9] mp 102–102.5°).

Separation and Identification of Isomers.—The crude mixture from the Meisenheimer reaction above was separated using a F & M Model 810 gas chromatograph with a 20-ft, $^{3}/_{8}$-in.-o.d. aluminum column filled with 15% SE-30 on Chromosorb W. The sample was dissolved in acetone and injected into the column which was set at 150°. The 2-chloro-1,5-naphthyridine fraction melted at 115–118° and the 4-chloro-1,5-naphthyridine melted at 103–104°. A mixture of the two synthetic isomers behaved exactly as did the crude product of the Meisenheimer reaction when introduced into the gas chromatograph. Infrared spectra of the separate isomers and the synthetic compounds were identical. There was no depression of melting point between synthetic and separated compounds; however, an approximately equal mixture of 2- and 4-chloro compounds melted in the range 72–93°.[10]

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[1] J. Meisenheimer, *Ber.*, **59**, 1848 (1926).

[2] B. Bobranski, L. Kochanska, and A. Kowalewska, *ibid.*, **71**, 2385 (1938).

[3] B. Bobranski, *ibid.*, **71**, 578 (1938).

[4] H. J. den Hertog and N. A. I. M. Boelrijk, *Rec. Trav. Chim.*, **70**, 578 (1951).

[5] E. V. Brown, unpublished results.

[6] E. P. Hart, *J. Chem. Soc.*, 1879 (1954).

[7] A. Albert, *ibid.*, 1790 (1960).

[8] V. Petrow and B. Sturgeon, *ibid.*, 1157 (1949).

[9] J. T. Adams, C. K. Bradshear, D. S. Breslow, S. T. Amore, and C. R. Hauser, *J. Am. Chem. Soc.*, **68**, 1317 (1946).

[10] All melting points are corrected.

Oxymercuration of Allenes[1]

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Several inconsistencies have emerged in studies of electrophilic addition to cyclic and straight-chain

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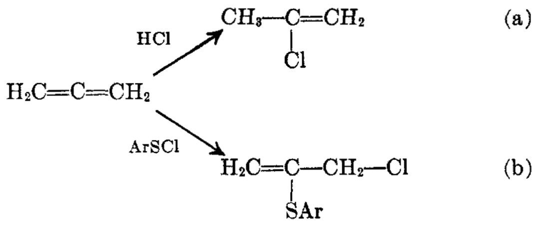
[1] From the Ph.D. Dissertation of R. K. Sharma, University of Texas 1964.

[2] (a) American Oil Co. Fellow, 1960; Dow Chemical Co. Fellow, 1961; (b) Department of Chemistry, University of Utah.

allenes. Jacobs and Johnson[3] observed that allene itself reacts with hydrogen chloride and with dinitrobenzenesulfenyl chloride to give products illustrating the two different possible modes of addition. The



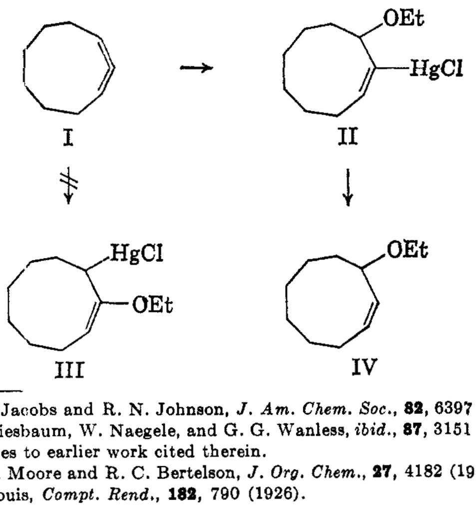
$$\mathrm{H_2C{=}C{=}CH_2} \xrightarrow{\mathrm{HCl}} \mathrm{CH_3{-}\underset{Cl}{\underset{|}{C}}{=}CH_2} \qquad \text{(a)}$$

$$\mathrm{H_2C{=}C{=}CH_2} \xrightarrow{\mathrm{ArSCl}} \mathrm{H_2C{=}\underset{SAr}{\underset{|}{C}}{-}CH_2{-}Cl} \qquad \text{(b)}$$

work of Griesbaum, *et al.*,[4] provides good evidence that the preferred site of protonation of allene is C-1 to give a vinyl carbonium ion and on this basis the hydrogen chloride addition pictured above may be considered the normal reaction for allene itself. The picture is further clouded by the observation[3] that 3-methyl-1,2-butadiene reacts with hydrogen chloride by reaction type b to give two isomeric allylic halides. Type-a addition was observed in the reaction between 1,2-cyclononadiene and benzenesulfenyl chloride.[5]

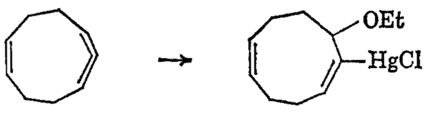
Allenes are reported to give a copious, white precipitate with ethanolic mercuric chloride and the reaction has sometimes been used as a test for the presence of an allenic linkage.[6-8] However, the nature of the product has never been determined. Because the oxymercuration reaction is rather well understood,[9] a study of the behavior of allenes under these conditions was undertaken.

The reaction of 1,2-cyclononadiene (I) with ethanolic mercuric chloride afforded a white, crystalline product. Only one of the two possible β-ethoxyorganomercury compounds expected (II and III) was found to be formed. Its structure was determined to be II on the basis of chemical and spectral data. Its infrared spectrum exhibited bands at 6.18 and 9.28 μ. Its nmr spectrum possessed signals at τ 4.91 (*J* = 7.8 cps, triplet, 1), 6.25 (multiplet, 1), and 9.05 (triplet, 3). The signal due to the methylene of the ethoxy group is a complex multiplet centered at τ 6.92. This increased multiplicity is undoubtedly due to magnetic asymmetry at C-2 of the ring.[10] Reduction of II using sodium-ammonia gave 3-ethoxycyclononene (IV), nmr signals at τ 4.49 (multiplet, 2), 8.89 (triplet, 3, *J* = 7 cps), 5.78 (multiplet, 1), and 6.58 (multiplet,[10] 2). It should be noted that the reduction of compound III would have given rise to an enol ether.



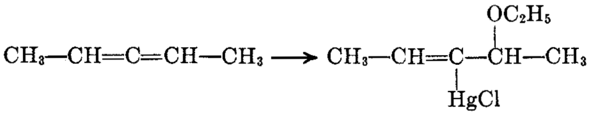
I II III IV

The oxymercuration of 1,2,6-cyclononatriene (V) took the same course as did I. The product (VI) had an infrared spectrum exhibiting bands at 6.08, 6.20, and 9.17 μ. Its nmr spectrum exhibited signals at τ 3.72 (multiplet, 1) and 4.16 (multiplet, 2), as well as those signals due to the ethoxy group.



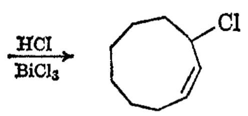
V VI

2,3-Pentadiene (VII), the only acyclic allene examined, underwent oxymercuration to give a liquid organomercury compound. Its infrared spectrum showed bands at 6.1 and 9.15 μ. The nmr spectrum possessed signals at τ 3.70 (quartet, 1), 6.01 (quartet, 1), 8.11 (doublet, 3), and other signals having the expected multiplicities and areas for the ethoxy group and the C-5 hydrogen atoms. It is thus clear that the organomercury compound is correctly formulated as 3-chloromercury-4-ethoxy-2-pentene (VIII) and that its formation is mechanistically identical with that of III and VI. The orientation of addition is type b, like that of hydrogen chloride to 3-methyl-1,2-butadiene but reversed from that of addition to 1,2-butadiene.[3]

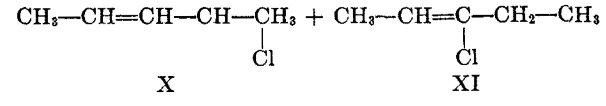


$$\underset{\text{VII}}{\mathrm{CH_3{-}CH{=}C{=}CH{-}CH_3}} \longrightarrow \underset{\text{VIII}}{\mathrm{CH_3{-}CH{=}\underset{HgCl}{\underset{|}{C}}{-}\overset{OC_2H_5}{\overset{|}{C}}H{-}CH_3}}$$

In order to more accurately compare oxymercuration with hydrogen chloride addition, the substrates studied in the former were also examined in the latter. Addition of hydrogen chloride, in the presence of catalytic bismuth chloride, to 1,2-cyclononadiene (I) gave only 3-chlorocyclononene (IX, type-b addition). Its nmr spectrum exhibited signals at τ 4.47 (multiplet, 2) and 5.12 (multiplet, 1). The similar reaction of 2,3-pentadiene (VII) was slightly more complex in that it gave a mixture of the two possible monoaddition products (X and XI). Nmr spectral data obtained from the mixture consisted of signals at τ 8.48 (doublet, 3, *J* = 7 cps), 8.32 (doublet, 3, *J* = 5 cps), 4.37 (multiplet), and 5.50 (multiplet). The areas of the τ 4.37 and 5.50 signals are in the ratio 2.18 thereby indicating the mixture to consist of X and XI in the ratio *ca.* 85:15. Thus, even though both products are formed, the principal one is that derived from type-b addition.



IX



$$\text{VII} \longrightarrow \underset{\text{X}}{\mathrm{CH_3{-}CH{=}CH{-}\underset{Cl}{\underset{|}{C}}H{-}CH_3}} + \underset{\text{XI}}{\mathrm{CH_3{-}CH{=}\underset{Cl}{\underset{|}{C}}{-}CH_2{-}CH_3}}$$

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[3] T. L. Jacobs and R. N. Johnson, *J. Am. Chem. Soc.*, **82**, 6397 (1960).

[4] K. Griesbaum, W. Naegele, and G. G. Wanless, *ibid.*, **87**, 3151 (1965), and references to earlier work cited therein.

[5] W. R. Moore and R. C. Bertelson, *J. Org. Chem.*, **27**, 4182 (1962).

[6] M. Bouis, *Compt. Rend.*, **182**, 790 (1926).

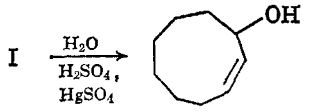
[7] G. F. Hennion and J. J. Sheehan, *J. Am. Chem. Soc.*, **71**, 1964 (1949).

[8] W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958).

[9] J. Chatt, *Chem. Rev.*, **48**, 4 (1951); T. G. Traylor, *J. Am. Chem. Soc.*, **86**, 244 (1964), and references cited therein.

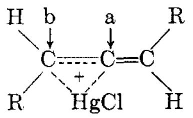
[10] G. M. Whitesides, D. Holtz, and J. D. Roberts, *ibid.*, **86**, 2628 (1964).

The hydration of terminal allenes by aqueous sulfuric acid in the presence of mercuric salts is known to proceed through type-a addition to give methyl ketones.[7,11] As expected on the basis of oxymercuration results cited earlier, 1,2-cyclononadiene (I) on refluxing in a solution of sulfuric acid, water, ethanol, and mercuric sulfate gave 3-ethoxycyclononene (IV) contaminated to the extent of about 1% with cyclononanone. The methyl ether was similarly obtained by the use of methanol in place of ethanol. Hydration of I in a solution of tetrahydrofuran, water, sulfuric acid, and mercuric sulfate afforded 3-hydroxycyclononene (XII) along with a trace of cyclononanone. Principal signals in the nmr spectrum of XII were found at τ 5.46 (multiplet, 1) and 4.56 (multiplet, 2).



XII

Although the results described do not permit an all-encompassing rationale for reported allene addition reactions, it is clear that the principal mode of addition of hydrogen chloride and alcohols (*via* oxymercuration) proceed in the same manner (type b) for simple 1,3-disubstituted cyclic or acyclic allenes. The attack of a nucleophile on the intermediate mercury complex derived from a 1,3-disubstituted allene is predominately b even though the orbital involved is orthogonal to the plane described by the p orbitals of the other double bond. To this extent, the reactions described are internally consistent.



The "anomalous" addition of benzenesulfenyl chloride to 1,2-cyclononadiene[5] could be the observation of kinetic rather than thermodynamic selectivity.[12] This aspect of the oxymercuration of allenes is presently under investigation.

Experimental Section

Boiling points and melting points are uncorrected. Infrared spectra were obtained with a Beckman IR-5 instrument using neat liquids or carbon tetrachloride solutions of solids. Vapor-liquid chromatographic analyses were made with an F & M Model 609 flame-ionization instrument equipped with a Carbowax 20 M column. Proton magnetic resonance spectra were obtained with a Varian Associates A-60 or DP-60 machine. Chemical shift and coupling constant measurements have an accuracy of τ ±0.02 and ±0.05 cps, respectively.

Oxymercuration of 1,2-Cyclononadiene (I).—To a solution of 6.97 g (0.0257 mole) of mercuric chloride in 34 ml of ethanol was added 3.0 g (0.025 mole) of 1,2-cyclononadiene.[13] The solution was stored at 30° for 4 hr and then at 0° for 10 hr. The white crystals (2.55 g) which had separated were removed by filtration. The filtrate was mixed with 100 ml of ether, and washed with saturated sodium chloride solution then with water, and finally with aqueous sodium bicarbonate solution. The organic phase was dried over anhydrous magnesium sulfate and freed of solvent at an aspirator. The residue was shaken with 15 ml of pentane to induce crystallization. Crystals so obtained were combined with the first crop (total 3.90 g, mp 113–114°). Recrystallization from petroleum ether (bp 30–60°) afforded pure 2-chloromercury-3-ethoxycyclononene (II), mp 117.5–118.0°.

Anal. Calcd for $C_{11}H_{19}ClHgO$: C, 32.76; H, 4.75. Found: C, 32.64; H, 4.92.

The filtrate was freed of solvent at an aspirator and distilled using a bath temperature of 50°. The distillate (0.85 g) was collected in a Dry Ice cooled trap and analyzed by vapor–liquid chromatography using several columns and authentic samples to establish identity of the components. It was found to consist of 94% 1,2-cyclononadiene and 6% 3-ethoxycyclononene.

Sodium–Ammonia Reduction of 2-Chloromercury-3-ethoxycyclononene (II).—A 1-l., three-necked flask was fitted with an inlet tube for ammonia and a large Dry Ice condenser to which was attached a mercury gas-release valve. About 500 ml of ammonia was distilled into the flask without prior purification. The organomercury compound (II, 40.3 g, 0.10 mole) was added to the ammonia followed by 150 ml of anhydrous ether. The mixture was stirred for 15 min and 6.9 g (0.33 g-atom) of sodium metal was added in small portions. The mixture was stirred for an additional 25 min before excess reductant was destroyed by the addition of solid ammonium chloride. Ammonia was allowed to evaporate and the residue was processed in the usual way by ether extraction. Evaporation of ether and fractional distillation of the product gave 12.0 g of 3-ethoxycyclononene (IV), bp 97–98.5° (18 mm), $n^{29}D$ 1.4695.

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.31; H, 11.85.

Ethoxycyclononane.—3-Ethoxycyclononene (IV, 3.0 g) was dissolved in 30 ml of methanol and hydrogenated over 10% palladium–charcoal. Removal of solvent and distillation gave 1.35 g of ethoxycyclononane, bp 99.5–100° (16 mm), $n^{29}D$ 1.4634. Its nmr spectrum exhibits a triplet (three protons) at τ 8.90 (J = 7 cps) and a quartet (two protons) at 6.62 (J = 7 cps).

Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.03. Found: C, 77.45; H, 12.84.

Addition of Ethanol to 1,2-Cyclononadiene (I).—1,2-Cyclononadiene (9.15 g, 0.075 mole) was dissolved in 12.0 g of ethanol and added to a solution of 6.0 g of concentrated sulfuric acid, 0.94 g of mercuric sulfate, 6.0 g of water, and 12.0 g of ethanol. The solution was heated under reflux for 40 min under a nitrogen atmosphere, cooled, and poured into ice–water. The product was isolated by extraction with pentane followed by the usual processing of the extracts. Removal of solvent at an aspirator and fractionation of the residue gave 9.0 g of 3-ethoxycyclononene (IV), bp 93–94° (16 mm), which was identical in all respects with a sample prepared from II. Vapor–liquid chromatography showed the product to be at least 99% pure.

Addition of Methanol to 1,2-Cyclononadiene.—A mixture of 1,2-cyclononadiene (I, 3.0 g, 0.025 mole), 6.0 g of methanol, 2.0 g of concentrated sulfuric acid, and 0.31 g of mercuric sulfate was allowed to react under a nitrogen atmosphere as described in the preceding experiment. Distillation of the crude product gave 2.15 g of 3-methoxycyclononene, bp 85–86.5° (16 mm), $n^{28}D$ 1.4730. Vapor–liquid chromatography showed that it contained about 1% of cyclononanone.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.72; H, 11.62.

Hydration of 1,2-Cyclononadiene.—1,2-Cyclononadiene (3.0 g) was dissolved in 10 ml of tetrahydrofuran and added to a solution of 2.0 g of concentrated sulfuric acid, 2.0 g of water, 0.31 g of mercuric sulfate, and 20 ml of tetrahydrofuran. The solution was heated under reflux for 40 min and processed as described for the oxymercuration reaction. Fractional distillation of the product gave 0.58 g of 3-hydroxycyclononene (XII), bp 100° (3.5 mm), $n^{32}D$ 1.4965. Its infrared spectrum displays bands at 2.93, 6.03, and 5.86 μ. Vapor–liquid chromatography showed that cyclononanone was present to the extent of 1%. The *p*-nitrobenzoate was prepared in the usual manner and recrystallized from ethyl acetate, mp 114°.

Anal. Calcd for $C_{14}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.58; H, 6.79; N, 5.07.

Addition of Hydrogen Chloride to 1,2-Cyclononadiene.—A slow stream of *dry* hydrogen chloride was passed through a suspension of 0.1 g of anhydrous bismuth chloride in 3.0 g of 1,2-cyclononadiene maintained at −70°. The mixture was stirred continuously during the process. The flow was discontinued when 0.95 g of hydrogen chloride had been added. Stirring was continued for 12 hr at that temperature and the mixture was then allowed to warm to room temperature. A small amount of anhydrous potassium carbonate was added and the mixture was stirred and fil-

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[11] M. Bouis, *Ann. Chim.*, **9**, 402 (1928).

[12] W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, **88**, 2866 (1966).

[13] L. Skattebøl, *Tetrahedron Letters*, **5**, 167 (1961).

tered. The filtrate was fractionated to give 1.85 g of the addition product, 3-chlorocyclononene (IX), bp 87–89° (16 mm), $n^{28}\mathrm{D}$ 1.5004.

Anal. Calcd for $C_9H_{15}Cl$: C, 68.12; H, 9.53; Cl, 22.35. Found: C, 67.60; H, 9.35; Cl, 23.10.

Oxymercuration of 1,2,6-Cyclononatriene.—1,2,6-Cyclononatriene (V)[12] (6.5 g, 0.054 mole) was added to a solution of 17.65 g (0.065 mole) of mercuric chloride in 85 ml of ethanol and allowed to stand for 12 hr. The resulting green solution was filtered to separate 2.3 g of mercury. The filtrate was dissolved in 300 ml of ether and washed with sodium chloride solution, then water and finally dried over anhydrous magnesium sulfate. The solution was concentrated to 150 ml when it began to deposit fluffy, colorless crystals. These were separated by filtration and the filtrate was concentrated to near dryness at an aspirator without heating. The residue was shaken with a small volume of pentane and filtered. In this way, 1.0 g of white solid, mp 145–155°, was obtained. It was purified by recrystallization from ether, mp 159–160°. The substance was shown by nmr and analytical data to be 1-chloromercury-9-ethoxy-1,5-cyclononadiene (VI).

Anal. Calcd for $C_{11}H_{17}ClHgO$: C, 32.92; H, 4.27; Cl, 8.84. Found: C, 32.77; H, 4.28; Cl, 9.03.

Pentane was removed from the filtrate at an aspirator and the residue was distilled through a short-path system under high vacuum into a receiver cooled to −60°. The distillate (1.90 g) was examined by vapor–liquid chromatography and found to consist of 61% starting material (V) along with six other substances varying from 3 to 17%.

Addition of Hydrogen Chloride to 2,3-Pentadiene.—Dry hydrogen chloride was bubbled through a mixture of 5.0 g of 2,3-pentadiene (VII) and 0.20 g of anhydrous bismuth chloride at −70°. The reaction mixture was kept at −70° for 48 hr and then allowed to warm to 0° to permit the escape of unreacted hydrogen chloride. Only 1.4 g was consumed. The mixture was stirred briefly with anhydrous potassium carbonate and then filtered. Fractionation of the filtrate gave 1.1 g of 4-chloro-2-pentene (X) and 3-chloro-2-pentene (XI), bp 58–59° (197 mm). The proton resonance spectrum suggested the mixture to have a X/XI ratio of 85:15.

Oxymercuration of 2,3-Pentadiene.—A mixture of 1.75 g (0.026 mole) of 2,3-pentadiene (VII), 7.7 g (0.028 mole) of mercuric chloride, and 40 ml of ethanol was stored at 0° for 10 hr. Use of the work-up procedure described for the preparation of II gave 4.15 g of liquid residue. Distillation afforded 3.0 g of 3-chloromercury-4-ethoxy-2-pentene, bp 141° (0.04 mm), $n^{32}\mathrm{D}$ 1.5385. The structure assignment is based on nmr and analytical data.

Anal. Calcd for $C_7H_{13}ClHgO$: C, 25.24; H, 3.93; Cl, 10.64. Found: C, 23.85; H, 3.94; Cl, 8.93.

Efforts to obtain better data were unsuccessful.

Acknowledgment.—The authors are indebted to the Robert A. Welch Foundation for the support of this work.

Senecio Alkaloids. Synthesis of Sarracinic Acid

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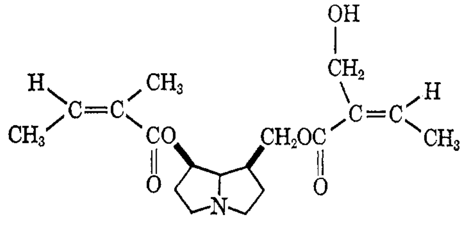
Received August 29, 1966

From the studies of Danilova, *et al.*,[2–5] and of Culvenor and Geissman,[6,7] the *Senecio* alkaloid sarracine has been formulated as platynecine esterified by the two pentanecic acids, angelic and sarracinic, as shown in I.



I

The assignment of the *trans* arrangement[8] of the hydrogen and carboxyl groups in sarracinic acid (2-hydroxymethyl-2-butenoic acid) derived from this alkaloid was made by correlation of the chemical shift of the vinyl proton with that published[9] on similar compounds.

The preparation of both geometric isomers of 2-hydroxymethyl-2-butenoic acid was undertaken for the following reasons: to establish by synthesis the structure of sarracinic acid; to test the correlation of Nair and Adams[9] which gave characteristic nuclear magnetic resonance (nmr) shifts for β-vinyl protons in stereomers of certain α,β-unsaturated acids; to study the interconversion of the two isomeric forms; and to see if the *cis* form would give mikanecic acid[6] (1-vinyl-3-cyclohexene-1,4-dicarboxylic acid) as does sarracinic acid. For these reasons, a synthesis yielding a reasonable ratio of the geometric isomers of 2-hydroxymethyl-2-butenoic acid was needed. Since House and Rasmusson[10] have shown that the product from reaction of a highly reactive ylid with an α-keto ester contained significant amounts of both geometric isomers, the use of the Wittig reaction was studied. The compound, ethyl acetoxypyruvate, required for this reaction had been prepared by Ratusky and Šorm[11] from the reaction of ethyl diazopyruvate with acetic acid and this α-keto ester on reaction with ethylidenetriphenylphosphorane gave, after the usual work-up, a mixture containing four compounds.

This mixture was separated by column chromatography and the isomeric ethyl 2-acetoxy-2-butenoates (II, III) were present in a 1:1 ratio and in a yield of 10%.

Hydrolysis of II gave a hydroxy acid (IV) identical with sarracinic acid,[12] and from III the isomeric *cis* acid V was formed. The *cis* acid has the higher melting point and is more stable than sarracinic acid. The olefinic proton[13] in sarracinic acid is at τ 3.60 and in V was found at 2.97. This is in line with the shift structure correlation published by Nair and Adams.[9] The substitution of a hydroxyl group for a hydrogen in the allylic position has only a small effect on the chemical shift of the olefinic proton.

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