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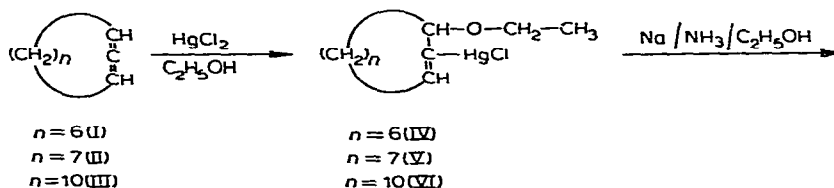
OXYMERCURATION OF CYCLIC ALLENES

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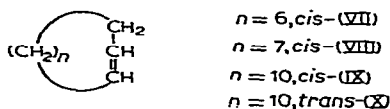
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Recent publications^{1,2} on oxymercuration reactions prompt us to report our study of the oxymercuration reaction of cyclic allenes, in which 1,2-cyclononadiene (I), 1,2-cyclodecadiene (II) and 1,2-cyclotridecadiene (III) were treated with mercuric chloride in ethanol solvent. The cyclic allenes were synthesized according to the procedure described by Moore and Ward³, and their properties agreed with those in the literature^{3,4}.



The reaction of each cyclic allene with neutral mercuric chloride in ethanol solvent gave a white crystalline product, the yield of which was increased by careful neutralization of the formed acid at the end of the reaction. The structures of the organomercury compounds were established on the basis of physical and chemical data as described below. Our results are in complete agreement with the structure assigned by Gardner and coworkers¹.



The melting points, percentage yield, analytical and IR data of the organomercury compounds are recorded in Table 1. As expected all the compounds show IR bands due to C=C and C-O stretching vibrations. In Table 2 are given the chemical shifts, *J* values, integrated areas and the assignment of protons. The 2-chloromercury-3-methoxycyclononene prepared from 1,2-cyclononadiene (I) and mercuric chloride in methanol gives a single line proton resonance spectrum for the methyl group, whereas it is known that methylene protons separated by one or two bonds are magnetically nonequivalent and display an A, B type of NMR spectrum⁵. This supports the proposal that the complex multiplet centered at $\tau \sim 6.5$ is due to the methylene of the ethoxy group.

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TABLE I

MELTING POINTS, YIELD, ANALYTICAL AND IR DATA

Compound	M.p. (°C)	Yield (%)	C(%) found (calcd.)	H(%) found (calcd.)	$\nu(\text{C}=\text{C})$ (cm^{-1})	$\nu(\text{C}-\text{O})$ (cm^{-1})
$\text{C}_{11}\text{H}_{19}\text{OHgCl}$	117-118	58	32.56 (32.76)	4.71 (4.75)	1623	1070
$\text{C}_{12}\text{H}_{21}\text{OHgCl}$	120	72	34.30 (34.61)	4.98 (5.02)	1626	1070
$\text{C}_{15}\text{H}_{27}\text{OHgCl}$	95-96	68	39.43 (39.25)	5.58 (5.66)	1618	1068

TABLE 2

NMR DATA

Compound	=CH- (τ)	-CH-O- (τ)	-O-CH ₂ - (τ)	-CH ₃ (τ)
$\text{C}_{11}\text{H}_{19}\text{OHgCl}$	4.21 $J \sim 8$ (t, 1) ^a	5.55 (bm, 1)	6.50 (cm, 2)	8.80 $J \sim 7$ (t, 3)
$\text{C}_{12}\text{H}_{21}\text{OHgCl}$	4.54 $J \sim 8$ (t, 1)	5.58 (bm, 1)	6.52 (cm, 2)	8.80 $J \sim 7$ (t, 3)
$\text{C}_{15}\text{H}_{27}\text{OHgCl}$	4.32 $J \sim 8$ (t, 1)	5.56 (bm, 1)	6.56 (cm, 2)	8.82 $J \sim 7$ (t, 3)

^a The numbers in parentheses give the number of protons; (m) = multiplet, (t) = triplet, (bm) = broad multiplet and (cm) = complex multiplet.

As further evidence for the structure of the organomercury compound we have shown that the reduction with sodium/ammonia/ethanol, a reagent which is known to cleave allylic carbon-oxygen bonds, gives cyclic olefin in good yield. Organomercuric compounds (IV) and (V) gave only *cis*-cyclononene [(VII)] and *cis*-cyclodecene [(VIII)], respectively, while the organomercuric compound (VI) gave a mixture containing 44% of *cis*- and 66% of *trans*-cyclotridecene [(IX) and (X)]. The formation of olefin(s) in the reduction reaction can be explained as due to the cleavage of the allylic ether in addition to the reduction of the C-Hg bond. These results are in agreement with our previous results on the metal/ammonia reduction of cyclic allenes⁶.

We have illustrated the synthetic utility of oxymercuration/demercuration reaction of cyclic allenes in the synthesis of α,β -unsaturated ketone from cyclic allene in two steps. The first step involves the oxymercuration reaction combined with the reduction of the oxymercurial intermediate by sodium borohydride *in situ* according to the recent procedure of Brown and Geoghegan⁷. This method provides a convenient method of hydrating cyclic allenes in a particular orientation. The second step in the synthesis involves mild oxidation of α,β -unsaturated alcohol with activated manganese dioxide to obtain α,β -unsaturated ketone in good yield. Details of this synthetic procedure will be published in a separate communication elsewhere.

EXPERIMENTAL

Boiling and melting points are uncorrected. IR spectra were obtained with a Perkin-Elmer Infracord Model 137B with sodium chloride optics in nujol or using thin film. Nuclear magnetic resonance spectra were taken on a Varian A-60 spectrometer in deuterated chloroform. Gas chromatographic analyses were made with Aerograph Model 90-P instrument using 5 ft by $\frac{1}{4}$ inch columns. The following liquid phases were employed (percentage by weight on 60/80 mesh Chromosorb W): 15% SE-30 silicone rubber, 15% Carbowax 20M-silver nitrate and 15% Ucon.

General oxymercuration procedure

The cyclic allene (0.05 mole) was added to a neutral solution of mercuric chloride (0.05 mole) in minimum amount of ethanol. The solution was shaken mechanically in nitrogen atmosphere till the precipitation of the organomercurial occurred (10–15 min). The precipitate was filtered and the filtrate was neutralized with sodium ethoxide to pH \sim 7, and the solution was shaken for one h in nitrogen atmosphere. The solution was concentrated and cooled when more white solid got separated. The solid was filtered, dried and combined with the first crop. Recrystallization from 95% ethanol afforded the pure organomercury compound.

Sodium/ammonia/ethanol reduction

The general procedure⁸ of sodium/ammonia/ethanol reduction was followed using each organomercuric compound (0.04 mole), sodium (0.80 g-atom), 200 ml of liquid ammonia and the required amount of absolute ethanol. The cyclic olefin was obtained in good yield, and its identity was established in each case by comparison of IR and gas chromatographic retention times on several columns with an authentic sample.

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