Reactions of 1,3,5-Hexatriene

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SEVERAL NEW derivatives of 1,3,5-hexatriene (*3*) were prepared. The Diels-Alder reaction products from acrylonitrile, acrolein and diethyl acetylenedicarboxylate were isolated and characterized. The reaction products from the reaction of hexatriene and dihalocarbenes were mono- and di-adducts. The carbene reaction with ethyl diazoacetate was also carried out. The reaction with perbenzoic acid gave only a monoepoxide. The products were characterized by means of carbon and hydrogen analyses, U.V. and I.R. spectra and conversion to known compounds, Table I.

LITERATURE CITED

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Table I. Derivatives of 1,3,5-Hexatriene

Compound	B.P./M.P.	Method of Prep.	Physical Constants
2-Vinyl-1,2,5,6-tetrahydrobenzonitrile	81-84°/6 mm.	A.	n^{24}_{D}1.4855
2-Vinyl-1,2,5,6-tetrahydrobenzaldehyde	83-86°/15 mm.	A.	n^{25}_{D}1.4898
Diethyl-3-vinyl-3,6-dihydrophthalate	170-171°/15 mm.	A.	n^{23}_{D}1.4920
1-(2,2-Dichlorocyclopropyl)-1,3-butadiene	86-88°/30 mm.	A.(*1, 5*)	n^{25}_{D}1.5207, $\epsilon_{235mu} = 26{,}400$
1,2-bis-(2,2-Dichlorocyclopropyl)-ethene	54.5-55.2°	B(*1, 5*)	
1-(2,2-Dibromocyclopropyl)-1,3-butadiene	58-62°/1 mm.	B(*1, 5*)	n^{23}_{D}1.5789, $\epsilon_{230mu} = 23{,}000$
1,2-bis-(2,2-Dibromocyclopropyl)-ethene	96-97°(Explodes above 100°)	B(*1, 5*)	
3-(2,2-Dichlorocyclopropyl)-1,2,3,6-tetrahydrophthalic anhydride[a]	133.5-134.5°	B(*1, 5*)	
3-(2,2-Dibromocyclopropyl)-1,2,3,6-tetrahydrophthalic anhydride[b]	85.5-86°	A.	
1-(2-Carbethoxycyclopropyl)-1,3-butadiene	58-60°/1 mm. (Polymerizes)	C(2)	n^{20}_{D}1.4855, $\epsilon_{235mu} = 22{,}500$
1,2-bis-(2-Carbethoxycyclopropyl)-ethene[c]	115-116°	C(2)	
1,2-Epoxy-3,5-hexadiene	57-58°/38 mm.	D(*4*)	n^{24}_{D}1.4937

Method A. Diels-Alder reaction with appropriate dienophile.
Method B. Dihalocarbene generated from haloform with potassium *tert*-butoxide.
Method C. Carbene reaction generated from ethyl diazoacetate.
Method D. From perbenzoic acid. Polymerizes unless diluted with chaser, before distillation.

[a] The corresponding acid was prepared by alkaline hydrolysis, m.p. 245-248°. [b] Same, m.p. 234-235°. [c] Same, m.p. 265-270°.

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Synthesis of Some New Aldoxime Derivatives

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4-PYRIDINECARBOXALDOXIME chloride was prepared by the method of Poziomek and Melvin (*2*). The chloride was allowed to react with excess hydroxylamine in methanol and the product was concentrated under reduced pressure. The recrystallized solid product was identified as 4-pyridinecarboxaldehydehydroxyamidoxime. In a similar reaction, the 2-pyridinecarboxaldoxime chloride was treated with hydroxylamine to give 2-pyridinecarboxaldehydroxyamidoxime. Properties are listed in Table I.

4-Pyridinecarboxaldoxime chloride was heated with sodium azide, in methanol, for thirty minutes. 4-Pyridinecarboxaldehydeaziodoxime was obtained by concentration and recrystallization. A similar reaction with 2-pyridinecarboxaldoxime chloride gave the corresponding isomeric azidoxime.

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