# The Reaction of Dichlorocarbene with Trimethylcyclopropene

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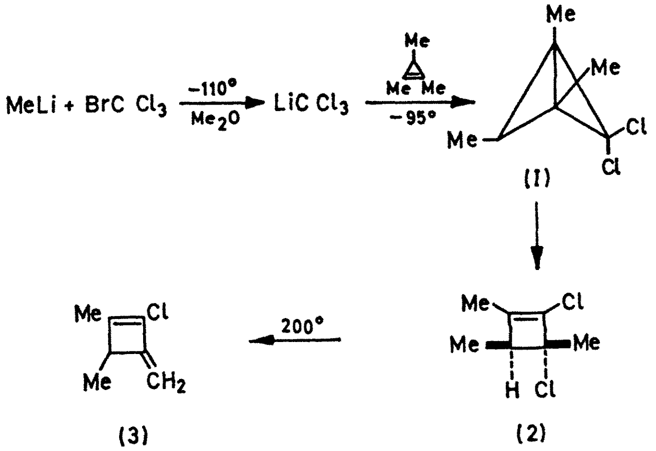
*Summary*. The reaction of dichlorocarbene generated from lithium trichloromethide with 1,2,3-trimethylcyclopropene produces 2,3-dichloro-*cis*-1,3,4-trimethylcyclobut-1-ene; even at −73° the presumed intermediate 4,4-dichloro-1,2,3-trimethylbicyclo[1,1,0]butane could not be detected.

THE availability of bicyclobutanes from 1,3-disubstituted cyclobutanes,[1] 4-diazobut-1-enes,[2] 1,1-dihalogenocyclopropanes,[3] and acetylenes[4] have made this fascinating ring system a useful intermediate for both synthetic and theoretical studies. Although many variously substituted derivatives are known, no report of a bicyclobutane substituted with halogens in the methylene positions appears. We were interested in such derivatives as possible synthetic precursors to tetrahedrane.[5]

The reaction of 1,2,3-trimethylcyclopropene[6] with lithium trichloromethide[8] (generated from bromotrichloromethane at −115°) in dimethyl ether solution at −95° gave a 74% yield of 2,3-dichloro-*cis*-1,3,4-trimethylcyclobutene (2) (see Scheme). The structural assignment was based on its elemental composition as $C_8H_{10}Cl_2$ (determined by high-resolution mass spectrometry) and its spectroscopic properties: i.r. ($CCl_4$) 1670 cm$^{-1}$, n.m.r. ($CCl_4$) $\delta$ 3·02, 1H, finely coupled quartet, $J$ 7 Hz; 1·70, 3H, doublet, $J$ 1·5 Hz; 1·54, 3H, singlet; and 1·11, 3H, doublet, $J$ 7 Hz. Irradiation of the doublets at $\delta$ 1·70 and 1·11 collapsed the signal at $\delta$ 3·02 to a sharp quartet and a broad singlet, respectively. It was further characterized by its ready dehydrochlorination to 1-chloro-2,3-dimethyl-4-methylenecyclobutene (3). The latter was also characterized by its elemental composition ($C_7H_9Cl$) as determined by high-resolution mass spectrometry and its spectroscopic properties: i.r. ($CCl_4$) 1695, 1623, and 860 cm$^{-1}$, n.m.r. ($CCl_4$) $\delta$ 4·60, 1H, finely coupled singlet; 4·46, 1H, finely coupled singlet; 3·02, 1H, quartet with further fine coupling, $J$ 7 Hz; 1·88, 3H, finely coupled singlet; and 1·15, 3H, doublet, $J$ 7 Hz.



SCHEME. *Reaction of* 1,2,3-*trimethylcyclopropene with trichloromethyl-lithium.*

The formation of the cyclobutene (2) is best rationalized in terms of an electrocyclic ring expansion of an intermediate bicyclobutane. Assuming initial dichlorocarbene attack from the less hindered face of 1,2,3-trimethylcyclopropene generates *exo*-4,4-dichloro-1,2,3-trimethylbicyclo[1,1,0]butane (1). Orbital symmetry considerations require that the *endo*-chlorine of (1) be the one to migrate.[9] This phenomenon has been observed in the dihalogenocyclopropane derived from norbornene among others.[10]

In an effort to detect the presence of bicyclobutane (1), an n.m.r. spectrum of the reaction solution was taken at −73° within 1 h of mixing the reagents at −95°. Only peaks attributable to the dichlorocyclobutene (2) were observed. On the assumption that the dichlorobicyclobutane (1) had a finite lifetime at −95°, n-butyl-lithium was added as a possible trapping agent immediately after mixing the cyclopropene with trichloromethyl-lithium. Again, only (2) was observed. The tremendous instability of (1) must result in part from the release of approximately 25 kcal/mole of strain energy in going from a bicyclobutane to a cyclobutene. Thus, it seems highly unlikely that an *endo*-2-halogenobicyclobutane will have any finite lifetime at most reasonable temperature ranges for synthetic purposes. Nevertheless, the facility of the reaction makes this route a useful synthesis of 3-chlorocyclobut-1-enes, potential precursors of cyclobutadienes.

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