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DICHLOROCARBENE GENERATION AND REACTIONS IN CATIONIC MICELLES IN AQUEOUS PHASE. Pt. I

CYCLO ADDITION TO ALKENES

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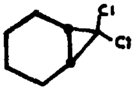
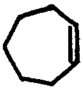
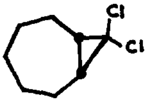
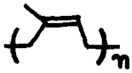
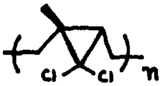
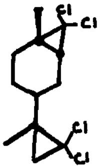
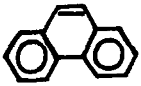
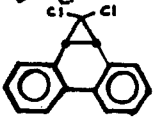
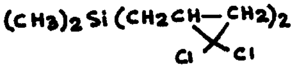
Dihalocarbenes have increasingly assumed the status of an important synthetic intermediate in organic chemistry. Their 2 + 1 ⟶ 3 cycloadducts with olefins offer useful routes to functionalized aromatics and ring expanded carbocyclics while adducts from aromatic ethers lead to tropolones[1,2]. Similarly adducts with enol ethers and esters of ketones are easily transformed into heterocyclics[2]. Several routes are available for generating dichlorocarbene[3] and it appears that its relative reactivity towards olefinic substrates is at least partly dependent on its mode and medium of generation. Amongst these methods, the generation of dichlorocarbene by the action of aqueous alkali on chloroform in presence of triethylbenzyl ammonium chloride (TEBA)[4] has attracted considerable attention. This method has been found superior to other methods in the synthesis of 1,1-dichlorocyclopropanes from less reactive olefins[5]. The TEBA method has also been used in an elegant stereoselective conversion of alcohols to halides by reaction with dichlorocarbene[6].

During the course of our investigations on a programme directed towards utilization of dichlorocarbene as an intermediate in bulk synthesis we discovered that TEBA is neither a unique nor the most efficient cationic micellar agent. In fact several cationic micellar agents catalyzed this reaction quite efficiently while anionic micelles strongly inhibited it. This study resulted in the development of a new procedure utilizing more efficient catalytic agents viz. cetyl trimethyl ammonium chloride (CTA) and the commercially available detergent cetrimide®, both of which are equally effective and work at a much lower concentration compared to TEBA.

By the present method even substrates such as phenanthrene and dimethyl diallysilane easily added dichlorocarbene to give the previously unknown 9,10 adduct[7] and the diadduct[8] respectively in 79 and 76% yields. The standard procedure is examplified below:

SUBSTRATE	PRODUCT	YIELD %
		98
		84
a. 		~100
	b. 	72
	c. 	79
$(CH_3)_2Si(CH_2CH{=}CH_2)_2$	d.  $(CH_3)_2Si(CH_2\underset{Cl\ \ Cl}{CH{-}CH_2})_2$	77

(a.) Natural purified Hevea rubber (ref.9). (b.) From (±) LIMONENE; B.P. 118–122°/0.3 mm, two forms isolated by fractional crystallisation, M.P. 99.6° and 128.5° (Mettler FPI) having identical behaviour in TLC. (c.) M.P. 140.2° (ref.7). (d.) B.P. 120°/0.4 mm, $\rho^{20°}_{4}$ 1.2152, $n^{20°}_{D}$ 1.4990 (ref. 8).

1,1-Diphenyl ethylene (8 g, 44 m mole), cetrimide® (116 mg, 0.44 m mole) and chloroform (11 ml, 135 m mole) were stirred at 30 ± 1°C while aqueous sodium hydroxide (13.5 g, in 27 ml ; 337 m mole) was added during 15 minutes. After 2 hours, iced water (50 ml) was added and the mixture acidified with sulphuric acid (10%) and extracted with ether (3 x 25 ml). The combined ether layer was washed with water, saturated sodium chloride, dried and solvent removed. This residual solid on recrystallization from ethanol yielded 1,1-diphenyl 2,2 -dichlorocyclopropane (11 g, 94%), m.p. 112° (Mettler FPI ; lit.[3(e)] 112 - 115°).

The liquid adducts were purified by fractional distillation through a vigreau column. Table lists representative preparations by this method.

All new compounds reported here were characterised by spectroscopy (I.R., N.M.R.) and gave correct elemental analysis.

For substrates which can tolerate alkali the present method offers considerable advantages because of commercial availability of the recommended catalyst, its efficiency at quite low concentrations and the ready adaptation of the method for up-scaling.

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