

DIHALOMETHANES AS C-H ACIDS IN THE CATALYTIC TWO-PHASE (CTP) SYSTEM -
A NEW METHOD FOR THE SYNTHESIS OF *gem*-DICHLOROCYCLOPROPANES¹

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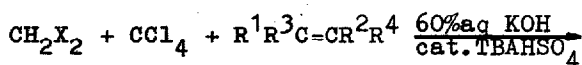
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Abstract: Dihalomethanes react with carbon tetrachloride and alkenes
in the CTP system affording *gem*-dichlorocyclopropanes.

Alkali metal hydroxides, in the presence of a quaternary ammonium salt as
a catalyst - catalytic two-phase, CTP, system - are the most convenient for
the deprotonation of haloforms and generation of dihalocarbenes². On the
other hand, very little is known about the applicability of this system for
the generation of dihalomethyl carbanions from the corresponding dihalometha-
nes. To the best of our knowledge, the only information³ deals with the H→D
exchange in dichloromethane, carried out in the presence of conc. NaOD/D₂O
and tetrabutylammonium hydrogen sulfate (TBAHSO₄) as catalyst.

We wish to report that dichloromethane (1a) stirred with carbon tetrachlo-
ride and alkene 2a-e (molar ratio 1.0:0.5:1.0), in the presence of 60% aq KOH
and TBAHSO₄ (6 mole %), afforded *gem*-dichlorocyclopropanes 3a-e. Under these
conditions, which were not optimized (r.t., 3h), the yields of 3 correspond
to the nucleophilicity of alkenes 2 (Scheme 1, Table).

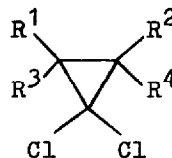
Scheme 1



1a, X=Cl

1b, X=Br

2a-e



3a-e

Reactions of 1a with hexachloroethane (HCE) and alkenes 2 under these condi-
tions, resulted in the formation of 3 in lower yields.

Table. Preparation of gem-dichlorocyclopropanes **3**

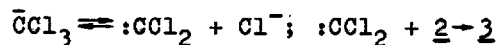
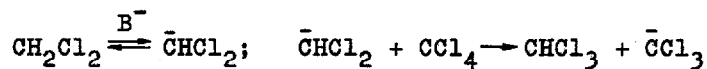
Entry	<u>2</u>	R ¹	R ²	R ³	R ⁴	<u>1</u>	<u>3</u>	
							No	yield ^a %
1	<u>2a</u>	Me	Me	Me	H	<u>1a</u>	<u>3a</u>	70
						<u>1b</u>		98
2	<u>2b</u>	Ph	H	Me	H	<u>1a</u>	<u>3b</u>	60
						<u>1b</u>		90
3	<u>2c</u>	H	H	(CH ₂) ₄		<u>1a</u>	<u>3c</u>	55 ^{b,c}
						<u>1b</u>		92 ^d
4	<u>2d</u>	Ph	H	H	H	<u>1a</u>	<u>3d</u>	35
						<u>1b</u>		95
5	<u>2e</u>	Bu	H	H	H	<u>1a</u>	<u>3e</u>	28
						<u>1b</u>		88

^aThe yields of isolated, pure products, calculated with regard to CCl₄; the molar ratio of 1a (or 1b):CCl₄:2=1.0:0.5:1.0 if otherwise not indicated; ^bWith 1a:HCE:2c=1.0:0.5:1.0 the yield is 23%; ^cAfter 36h the yield is 130%; ^dAfter 16h the yield is 115%.

After longer reaction time, the yields of products exceed 100% (e.g. 3c). This indicates that both 1a as well as carbon tetrachloride are the source of :CCl₂.

These results show that 1a is deprotonated in the CTP system to its carbanion, which enters the halogenophilic reaction⁴ with carbon tetrachloride affording chloroform and $\bar{\text{C}}\text{Cl}_3$. $\bar{\text{C}}\text{Cl}_3$ and chloroform after deprotonation, are the source of :CCl₂, which then adds to 2 giving the products 3 (Scheme 2).

Scheme 2



We have recently shown⁵ that carbon tetrachloride, when stirred in the CTP system with alkenes, affords 3. However, this reaction, carried out under the above mentioned conditions, afforded 3 in low yields (e.g. 3c, ca. 10%). Therefore, this alternative route of formation of 3 is of little importance.

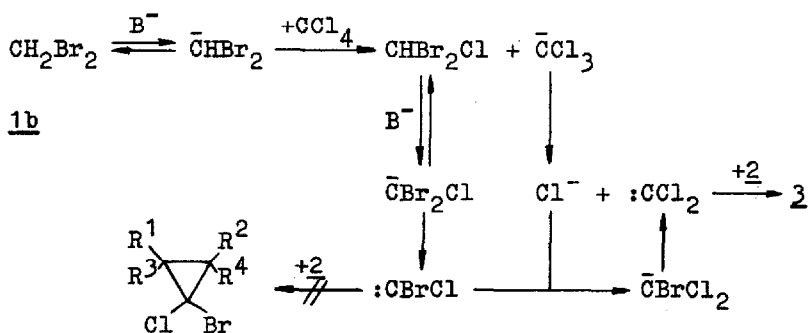
Recent investigations⁶ indicate that haloforms are efficiently halogenated by perhalomethanes or HCE in the CTP system, under sonication, generating species, which react with alkenes to give mixtures of gem-dihalocyclopropanes.

It may have been expected that the reaction of dibromomethane (1b)⁷ with carbon tetrachloride and 2 will afford gem-bromochlorocyclopropanes in high yields, perhaps contaminated with 3. However, much to our surprise, this reaction, carried out under the mentioned conditions, leads mainly to the formation of 3, while the expected gem-bromochlorocyclopropanes are formed in yields not exceeding 0.5% (Scheme 1, Table). The reaction of 1b, carbon tetrachloride and 2c, carried out under slightly different conditions (yield of 3c 115%, Table) shows that :CCl_2 is generated from both, carbon tetrachloride as well as 1b. This requires 1b to be transformed into bromodichloromethane and $\bar{\text{C}}\text{BrCl}_2$, which is presumably the precursor of :CCl_2 . In other words, the Br \rightarrow Cl exchange has to take place in the bromine containing species. We noted that the reaction of dibromochloromethane with 2c and an equimolar amount of triethylbenzylammonium chloride (TEBACl) as the source of lipophilic Cl^- ions, afforded an increased amount of 3c, as compared to the reaction carried out with a catalytic amount of TEBACl¹⁰.

Furthermore, equilibria between dihalocarbenes and halogen anions were suggested to exist in a mixture of haloforms^{10,11} or in a haloform-halide anion mixture¹² when these are stirred in the CTP system.

In order to explain our results, we temporarily assume that the reaction of :CBrCl with Cl^- is much faster than its addition to 2 (Scheme 3).

Scheme 3



Under modified conditions, our method is competitive in relation to other syntheses of gem-dichlorocyclopropanes¹³. Thus, 1a, stirred with an excess of carbon tetrachloride and 2a or 2c (1a : CCl₄ : 2 = 1.0:2.0:1.0) at 18–20°C for 4h, affords 3a or 3c in yields of 86% and 80%, respectively.

The mechanism as well as preparative aspects of the title reactions are presently investigated and will be reported in the future.

Acknowledgement. We thank the Polish Academy of Sciences for financial support of this work, Grant CPBP No 01.13.

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(Received in UK 10 July 1989)