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CHEMISTRY OF THE BICYCLOPROPENYL SYSTEM

I. FRAGMENTATION vs. REARRANGEMENT BY HALOGENATION [1)]

R. Weiß and H.P. Kempcke

Institut für Organische Chemie der Universität München

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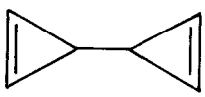
It was not until very recently[2)] that the bicyclopropenyl system 1 was recognized to complete the set of benzene valence isomers of the $(CH)_6$ type 2 - 4:



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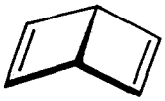

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In contrast to the other members of this set much of the chemistry of 1 resp. its derivatives[3)] remains to be explored. Recently we have established the mechanism of the Ag^{I}-catalized bicyclopropenyl rearrangement of the type 1 → 4[4)]. This work stimulated us to investigate the interaction of the bicyclopropenyl system with various other electrophiles so as to find out whether they proceeded according to the same mechanistic principles as described in ref. 4). In this paper we describe as a model case the course of bromination of 5a and 5b at ambient temperatures.

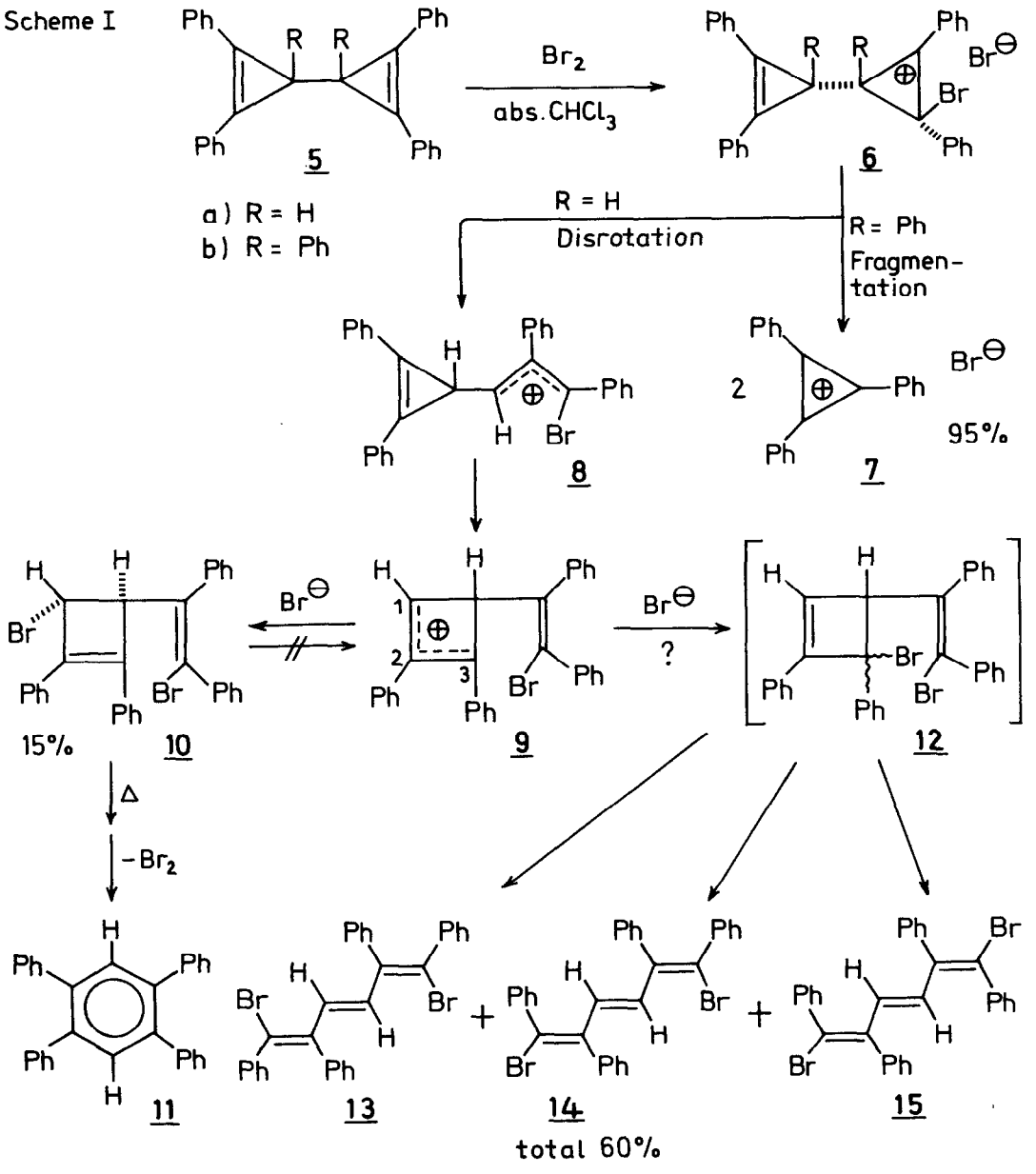
Addition of equimolar amounts of Br_2 to 5a in abs. $CHCl_3$ yielded cpds. 10 and 13 - 15 contained in the table together with their relevant data. Besides some polymeric material no other product could be detected.

With 5b, under the same reaction conditions, the cyclopropenium salt 7 was exclusively formed (cf.loc.cit. 3)). Scheme I accounts for these diverging results:

Electrophilic attack of bromine on 5 generates the intermediate 6 which

is faced with the alternatives of electrocyclic ring opening or fragmentation. With R=Ph the latter possibility is exclusively realized as fragmenta-

Scheme I



tion of 6 into 7 is strongly favoured by two complementary factors:

a) the well-known high stability of the triphenylcyclopropenium cation and

b) steric hindrance of disrotatory ring opening modes in 6 (model). With these two factors missing (R=H) 6 collapses to 8 (sterically most favourable disrotation) followed - or accompanied - by ring enlargement of the cyclopropenylmethyl cation → cyclobutenyl cation type[4]. Finally the key intermediate 9 adds $Br^{\oplus}$ in 1-position stereospecifically from the sterically least hindered side with formation of the vinyl-cyclobutene 10.

When heated beyond 150° in the solid state 10 rearranges to 11 with concomitant elimination of Br_2. The most plausible mechanism for this transformation involves an electrocyclic vinylcyclobutene-hexatriene-cyclohexadiene sequence with subsequent loss of Br_2.

The main product of bromination, however, is a mixture of stereoisomeric α,ω-dibromo-hexatrienes 13 - 15 which were obtained in pure form by fractional crystallization (cf. table).

Table

cpd.	yield	mp. °C	IR (KBr)	UV (Dioxane)		NMR (TMS, $CDCl_3$)
				λ_{max}	ε	
10	15%	145° (dec.)	—	303	17800	τ = 5.0 (1H,d) τ = 5.5 (1H,d) J_{HH} = 1.1 Hz
13	15%	206°	ν-CH=CH- (trans) 980 cm^{-1}	336	31000	τ = 4.02 (2H,s)
14	35%	162°	"	336	34500	τ = 3.35 (1H,d) τ = 3.80 (1H,d) J_{HH} = 15.5 Hz
15	10%	225°	"	339	38600	τ = 3.08 (2H,s)

Topologically cpds. 13 - 15 may stem from addition of $Br^{\oplus}$ to the 3-position of intermediate 9 and conrotatory ring opening of vinylcyclobutene 12 under the reaction conditions[5]. However, various arguments can be raised against this interpretation:

1) There is no convincing reason for a significantly higher stability of 10

(isolated) as compared to 12 (not observed).

2) Control experiments showed that 10 does not experience a 1,3-bromine shift to yield cpds. 13 - 15 (via 10) under the reaction conditions. Therefore, the observed ratio 10/13-15 (cf. table) must reflect the relative tendencies of 9 to add $Br^{\oplus}$ in 1- or 3-position respectively. This is in contrast to the expectation that an intermediate of type 9 should exhibit a strong preference for nucleophilic addition in 1-position[4].

In view of these arguments it is therefore quite likely that there exists an alternative pathway of bromination - probably radical in nature - which is responsible for the formation of most of cpds. 13 - 15. Experiments concerned with this problem are in progress.

In summary we come to the conclusion that Br_2-induced rearrangement of 5a - to the extent that it is ionic - is associated with the same topological pattern as the Ag^{I}-catalyzed bicyclopropenyl rearrangement[4]. The same holds for HX-additions and certain types of cycloaddition[6].

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LITERATURE

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2) Lawrence T.Scott and M.Jones,Jr., Chem.Rev. 72 (2), 181 (1972)

3) The parent compound is unknown. Derivatives: R.Breslow, P.Gal, H.W.Chang and L.J.Altmann, J.Amer.Chem.Soc., 87, 5139 (1965)

4) R.Weiß and St.Andrae, Angew.Chem., Int.Ed.Engl. 12 (2), 150,153 (1973)

5) In this context, no mechanistic conclusions can be drawn from the stereo-chemistry of compounds 13 - 15 because Br_2-induced cis-trans-isomerizations cannot be excluded under the reaction conditions.

6) R.Weiß and H.P.Kempcke, to be published.