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CHLORINE CIS-ELIMINATION OF A DIARYL-1,2-DICHLOROETHYLENE WITH BASE

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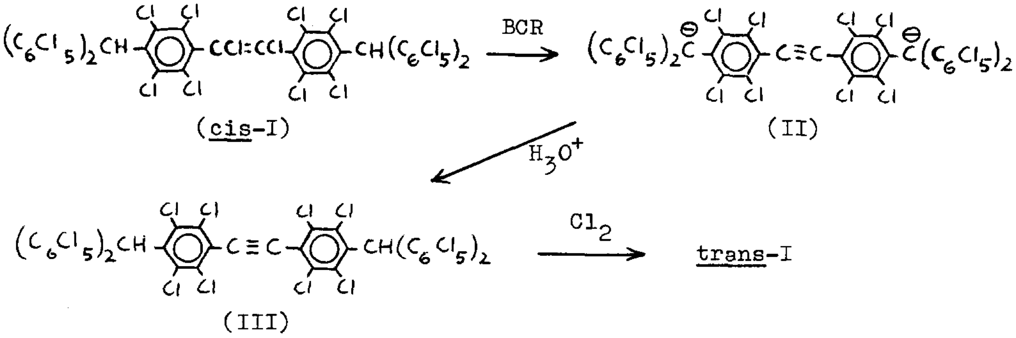
The so-called αH-quasiperchlorocompounds are most convenient precursors for the synthesis of inert perchlorocarbon radicals.[1] It was expected, therefore, that the *cis*- and the *trans*-αH,α'H-triacontachlorovinylenebis-4-triphenylmethane (I) with NaOH in ethyl ether-DMSO (reagent BCR) would give the corresponding dicarbanions, which by treatment with iodine would finally yield the *cis*- and the *trans*-perchlorovinylenebis-4-triphenylmethyl radicals, respectively, as in the synthesis of perchloro-α,α,α',α'-tetraphenylbi-*p*-tolyl-α,α'-ylene (PerchloroChichibabin biradical).[1]

The authors wish now to report that the reaction of *cis*-I with reagent BCR, at room temperature, gives an intense blue solution of perchloroethynylenebis-4-triphenylcarbanion (II) which, on treatment with aqueous HCl, yields αH,α'H-octacosachloroethynylenebis-4-triphenylmethane (III, 61.9%), mp 392-5º (dec.), showing, surprisingly, that *cis*-elimination occurs readily with the base.

Anal. Calcd. for $C_{40}H_2Cl_{28}$: C, 32.6; H, 0.1; Cl, 67.3. Found: C, 32.5; H, 0.2; Cl, 67.2. *ir* (KBr) ν 2920 (w)(αH), 1525 (w)(1st arom.), 1435 (w), 1370 (s)(2nd arom.), 1348 (s)(id.), 1330 (s)(id.), 1319 (s)(id.), 1303 (s)(id.), 810 (s), 710 (m), 680 (m), 660 (m) cm^{-1}. *uv* (cyclohexane) $\lambda(\varepsilon)$ 220 (175,000), 306 (31,000), 320 (46,000), 325 (38,000; sh), 343 (48,000) nm.

By treatment with reagent BCR, under the same conditions, *trans*-I gives a mixture of *trans*-ethylene dicarbanion and dicarbanion II (ratio 2:1). III adds chlorine in the presence of iodine or on illumination with white incandescent light giving *trans*-I (94.4 and 98.4% yields, respectively).



(*cis*-I) (II) (III) *trans*-I

It is known that reagent BCR can act as an electron donor towards chemically inert, electron active carbon free radicals.[1] It is therefore suggested that the initial essential step of the vicinal dechlorination is the release of an electron to an antibonding π-orbital of the ethylene system forming a reactive radical-anion, the following changes then taking place:

$$\begin{tikzcd}
\underset{(\textit{cis}\text{-I})}{\mathrm{ArCCl{=}CClAr}} \arrow[r, "+e", "(1)"'] & (\mathrm{ArCCl{=}CClAr})^{\ominus\bullet} \arrow[r, "-\mathrm{Cl}^-", "(2)"'] & \mathrm{Ar\dot{C}{=}CClAr} \arrow[dl, "+e"', "(3)"] \\
\underset{(\mathrm{III})}{\mathrm{ArC{=}CAr}} & \mathrm{Ar\overset{\ominus}{C}{=}CClAr} \arrow[l, "-\mathrm{Cl}^-"', "(4)"] &
\end{tikzcd}$$

A similar mechanism has been suggested for the electrolytic reduction of perchlorostyrene giving ω*H*,4*H*-tetrachlorophenylacetylene.[2] It is assumed that *cis*-I eliminates chlorine much more readily than *trans*-I because step 1 is more favored on account of the ethylene system being less shielded to approach of the electron donor. This is, however, a conjectural matter.

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