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FREE-RADICAL ADDITION OF $BrCCl_3$ TO 1-DECENE INITIATED BY TETRAHYDROFURANE

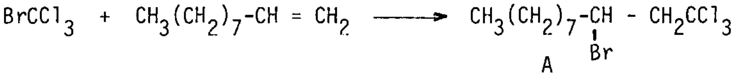
M. HEINTZ, G. LE NY and J.Y. NEDELEC*

C.N.R.S., GR n° 12, 2, rue H. Dunant, 94320 THIAIS (France)

Summary : *Kharasch addition of $BrCCl_3$ to 1-decene and spin-trapping ESR observations show that $BrCCl_3$ is spontaneously reduced in THF.*

Polyhalogenated compounds (CCl_4, $BrCCl_3$, CF_2Br_2...) are reduced by single electron transfer from organic nitrogen or sulfur compounds, but sofar such reaction has not been pointed out for ethers[1,2].

We have found that commercial THF (purity > 99.5 %) promotes the Kharasch addition of $BrCCl_3$ to 1-decene at room temperature even in the dark



$$BrCCl_3 + CH_3(CH_2)_7\text{-}CH = CH_2 \longrightarrow CH_3(CH_2)_7\text{-}\underset{Br}{CH} - CH_2CCl_3$$

A

$BrCCl_3$ (1.2 ml, 0.02 mol) and 1-decene (1.9 ml, 0.01 mol) were stirred for 6 hrs at room temperature in 25 ml of THF in the dark, in air or under argon, to give A in 50 % yield (GLC) and less than 5 % of the non-brominated products B and C[3].

$R\text{-}CH_2 - CH_2 - CCl_3$ B

$R - CH = CH - CCl_3$ C

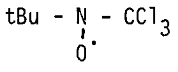
Products were isolated and identified by comparison (GLC, ^1H NMR) with authentical samples obtained from the peroxyde initiated addition of $BrCCl_3$ to 1-decene (A and C), and of $HCCl_3$ to 1-decene (B).

This experiment was repeated several times and with THF's of various origins[4]. Every time A was the main product (30 %-50 % yield determined by GLC) but the rate of its formation (from 1 to 12 hrs)[3] was found to depend on the batch of THF.

In pentane instead of THF no reaction took place. At 40°C the reaction was accelerated (average factor 3) and we obtained A and B in 20 % yield each.

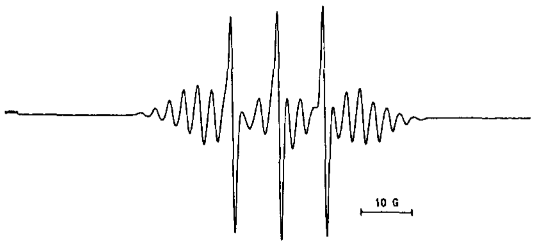
On irradiating the mixture with a 250 W sun lamp at 25° C the rate of formation of A was increased (factor 6) without change in the yields of the products ; it was checked that the addition did not occur in pentane.

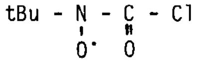
We have also made the following ESR observations. When we added 0.5 cm³ of $BrCCl_3$ to 1 cm³ of THF in the presence of tBuNO at room temperature we very rapidly obtained the typical complex signal of radical D (a_N = 13.87 G ; a_{Cl} = 2.53 G ; g = 2.0069) which slowly evolved into the simple 1:1:1 triplet (a_N = 7.6 G ; g = 2.0074) usually attributed to E[5]. After 15 minutes both radicals were observed simultaneously as shown on the figure.



$\text{tBu} - \underset{\text{O}^{\bullet}}{\text{N}} - \text{CCl}_3$

D





$\text{tBu} - \underset{\text{O}^{\bullet}}{\text{N}} - \underset{\text{O}}{\overset{}{\text{C}}} - \text{Cl}$

E

Figure : ESR spectrum of the two nitroxides D and E formed in the reaction of THF and $BrCCl_3$ in cyclohexane in the presence of tBuNO after 15 minutes at room temperature.

The nature of the adduct as well as the ESR observations clearly indicate that we are dealing with a free-radical process involving the formation of $^{\bullet}CCl_3$. So, even if the nature of the donor remains to be unequivocally specified, the initiation step of the chain addition certainly is a single electron reduction of the carbone-bromine bond in $BrCCl_3$.

REFERENCES

1. J.A.K. HARMONY in "Methods in Free-Radical Chemistry", E.S. HUYSER Ed., Vol. 5, chap. 2, M. Dekker Inc., New-York, 1974.
2. I. RICO, D. CANTACUZENE and C. WAKSELMAN. J. Org. Chem., 1983, 48, 1979, and references cited therein.
3. Reactions were followed by GLC using internal standard and stopped at the maximum yield of A. Yields were not optimized.
4. Three THF's have been tested and used as received and freshly distilled over Na/benzophenone : i) from SDS (Solvants Documentation Synthèse, Peypin, France) : ">99.5 % stabilized with 50 ppm ionol" ; ii) from Janssen Chimica (France) : "99.9 % with <0.025 % of BHT" ; iii) from Ega-Chimie (France) : "spectrophotometric grade 99.5 %, free of inhibitor".
5. M. J. PERKINS in "Advances in Physical Organic Chemistry", vol. 17, p. 1, V. GOLD and D. BETHELL Ed., Academic Press Inc., London, 1980.

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