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FREE RADICAL ADDITIONS TO BENZONORBORNADIENE

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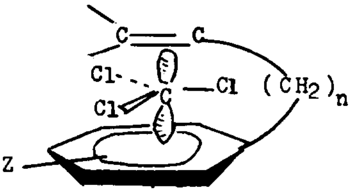
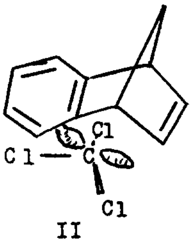
Martin and Gleicher (1) have reported an unusually large substituent effect in the free radical addition of bromotrichloromethane to meta and para substituted 3-phenyl-1-propenes. The mechanism proposed for the addition involves the trichloromethyl radical in a pi complex with the aromatic ring I. This proposed mechanism leads to an interesting speculation regarding the mode of free radical addition to benzonorbornadiene (2).



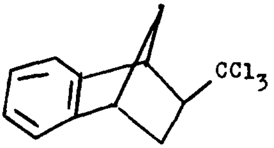
I



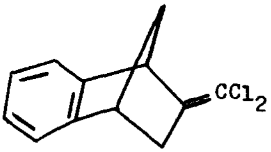
II

If an intermediate pi complex is formed, the attack of the trichloromethyl radical on the double bond would be on the endo side of benzonorbornadiene II.

Free radical addition of chloroform (3), using benzoyl peroxide as an initiator, gave a 40% yield of monomeric product and 60% telomers. Calculations from the molecular weight and carbon, hydrogen analysis data reveal that the telomeric product is 39% dimer and 61% trimer. The crystalline monomer (m.p. 49.5 - 50°) was shown by gas liquid chromatography (gl.c.), thin layer chromatography (t.l.c.), and proton magnetic resonance (p.m.r.) to be a single isomer (4). The product was shown to be *exo*-2-trichloromethylbenzonorbornene III by its p.m.r. spectrum and that of its dehydrochlorinated compound, 2,α,α-dichloromethylbenzonorbornene IV (5).

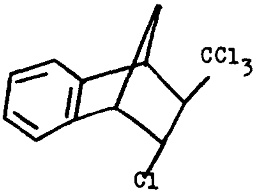


III

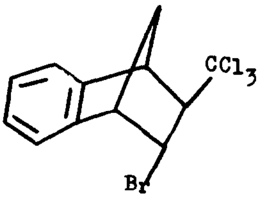


IV

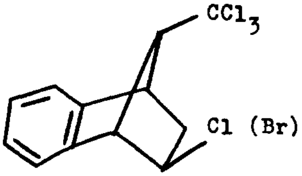
Carbon tetrachloride addition with benzoyl peroxide as an initiator gave a 45% yield of a single monomeric product. The monomer was shown to be *exo*-2-trichloromethyl-*endo*-3-chlorobenzonorbornene V. Bromotrichloromethane addition gave a product of similar structure VI in 95% yield.



V

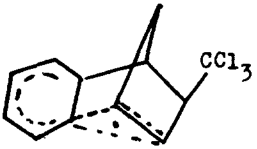


VI

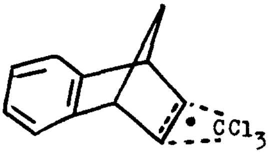


VII

It is obvious that a *pi* complex has not been an important intermediate in these reaction sequences. We are therefore obliged to propose an alternative intermediate for these reactions. The absence of rearranged product VII eliminates the possibility of the symmetrical homobenzylic radical VIII (or non-classical radical) as being either an intermediate or a transition state between two rapidly equilibrating classical radicals. At first glance the *trans* addition of $BrCCl_3$ and CCl_4 seems to require a bridged intermediate IX. However, space requirements for the trichloromethyl group and the halogen are probably too great to allow both groups to be in the *exo* position. *Trans* addition would undoubtedly take place even if a bridged intermediate were not

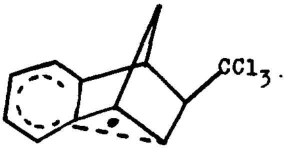


VIII

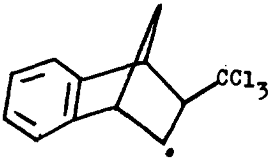


IX

operative. The data neither support nor rule out the unsymmetrical homobenzylic radical intermediate X. All of the data can be explained on the basis of a classical radical intermediate XI with the sterochemistry of the products being determined by the steric interactions between the olefin or the intermediate radical and the addend.



X



XI

We are currently studying substituent effects on these reactions in order to determine in more detail the mechanism of these reactions.

ACKNOWLEDGMENT

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REFERENCES

1. M.M. Martin and G.J. Gleicher, J. Am. Chem. Soc., 86, 233. 238 (1965).
2. G. Wittig and E. Knauss, Ber., 91, 895 (1958).
3. D.J. Trecker and J.P. Henery, J. Am. Chem. Soc., 85, 3205 (1963).
4. A detailed paper on the p.m.r. spectra of compounds of this type will be forthcoming.
5. New compounds described in this communication gave satisfactory elemental analytical and infrared data.