INFLUENCE OF A FREE RADICAL SUBSTITUENT ON REACTIVITY (REVERSE EFFECT). RESULTS INVOLVING BENZYLIC SYSTEMS

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<u>Summary</u>: The first examples of the influence of the free radical character on the reactivity of a non-radical substituent in the radical molecule (reverse effect) are reported. They include thermolysis, reductive dimerization and bromination, involving radicals related to perchlorotriphenylmethyl.

Since the discovery of the free radicals,¹ the effect of the substituents on their reactivity has been one of the most intensively studied subjects in Organic Chemistry. However, there exists no information whatsoever on the opposite effect; <u>i.e.</u>, the influence of the radical character on the reactivity of non--radical substituents. The study of such influence, the "reverse effect", has been almost an impossible aim since the radical character is usually the main drive for reactivity in free radicals. However, with the discovery of the so--called "inert free radicals" (IFR)² such type of studies have become possible; in fact, their radical character remains unchanged even <u>vs</u>. aggressive chemicals² and under rather strong reaction conditions.^{3,4} Many IFRs withstand temperatures as high as 300° in the air, and their half-lives in solution are of the order of a century.² The reasons (steric) for such inertness have been established.²

The first clear-cut examples of that influence are described next.

1) <u>Thermolyses</u>. A spectacular rate effect is observed in the homolyses (in solution) of benzyl halides



While $\alpha \underline{H}$ -compounds $\underline{3}$, $\underline{4}$ and $\underline{5}$ do not decompose up to 180° , radicals $\underline{1}$ and $\underline{2}$ yield biradical $\underline{7}$ at temperatures of 165° and 110° , respectively. Attempts to obtain the tetradecachloro-4-(iodomethyl)triphenylmethyl radical at -20° lead instead to the would-be product of its homolysis; <u>i.e.</u> biradical $\underline{7}$.

Biradical $\underline{7}$ is presumably formed by dimerization of the resulting singlet or biradical <u>p</u>-xylylene <u>6</u>.

Figure 1 accounts for the stabilization of the transition state for radicals $\frac{1}{2}$ or $\frac{2}{2}$ in terms of two molecular moieties. The corresponding moieties in αH ---compounds $\frac{3}{2}$, $\frac{4}{2}$ and 5 are almost non-interacting.

^{*} Related reactions giving radicals from singlet p-quinonoid species have been reported.^{4,5}



TRANSITION STATE FOR THE RADICAL

Figure 1. Simplified frontier-orbital interaction diagram concerning the homolysis of radical $\underline{1}$ or $\underline{2}$.

2) <u>Reductive dimerization</u>. The same spectacular effect is observed in the reduction of bromomethyl radical $\underline{2}$ with SnCl₂ giving biradical $\underline{7}$, presumably also through <u>p</u>-xylylene <u>6</u>. Under the same conditions <u>aH</u>-bromomethyl compound <u>4</u> does not react.

3) <u>Bromination</u>. A competitive, AIBN induced bromination of tetradecachloro--4-methyltriphenylmethyl radical ($\underline{8}$) and $\underline{\alpha}\underline{H}$ -tetradecachloro-4-methyltriphenylme thane ($\underline{9}$) showed that the former reacts eight times faster than the latter.

Reasonable propagation steps for bromination of radical $\underline{8}$ are

$$(C_{6}Cl_{5})_{2}C \xrightarrow{C1 \quad C1} CH_{3} + Br \xrightarrow{step 1} [\underline{6}]$$

$$\overset{8}{=} C1 \quad C1$$

$$[\underline{6}] + Br_{2} \xrightarrow{step 2} \underline{2} + Br$$

There is no firm basis for ascertaining whether step 1 or step 2 is rate-determining. In any case, steady-state considerations indicate that hydrogen-atom abstraction is favoured in radical $\underline{8}$ over that in <u>aH</u>-compound $\underline{9}$, where it is likely that such abstraction be rate-determining.

The rate enhancements referred to in 2) and 3) may be accounted for by assuming frontier-orbital interaction diagrams analogous to that of Figure 1.

In conclusion, in the preceding examples of the <u>reverse effect</u> the radical character does modify (accelerates) the reaction rates, and even allows reactions which, under given conditions, would not occur otherwise.

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(Received in UK 27 July 1982)