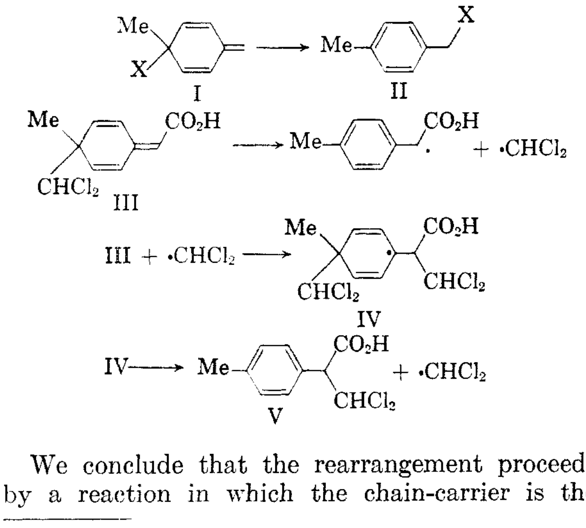
Communications TO THE EDITOR

The Mechanism of the von Auwers Rearrangement of Derivatives of 4-Methyl-4-polyhalomethyl-1-methylenecyclohexa-2,5-diene

Sir:

The rearrangement of the "semibenzenes" I (X = $CHCl_2$ or CCl_3) and their derivatives to the aromatic isomers II, discovered by von Auwers,[1] has tentatively been assigned an ionic mechanism.[2] We now present evidence to show that, at least in the case of the acid[3] III, the rearrangement involves a free-radical chain reaction.

The kinetics of the rearrangement of III to V have been measured spectrophotometrically in 20% (v/v) aqueous ethanol. The reaction exhibits a temperature-dependent induction period, and then obeys first order kinetics. From the change in length of the induction period with temperature between 130° and 152° an activation energy can be calculated for the initiation reaction of about 40 kcal./mole, which is of the expected order of magnitude.[4] Addition of benzoyl peroxide reduces the induction period without affecting the subsequent reaction. The rearrangement is inhibited by duroquinone. Ultraviolet irradiation of a solution of the triene III in petroleum ether yields the rearranged acid V even at room temperature.



We conclude that the rearrangement proceeds by a reaction in which the chain-carrier is the dichloromethyl radical. Other 4-halomethylsemibenzenes (I; X = CCl_3, $CHBr_2$, or CBr_3) appear to isomerize by an analogous process. The postulated intermediate radical IV is interesting, since it has the same electronic structure as the intermediate in radical aromatic substitution.

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(1) K. v. Auwers and G. Keil, *Ber.*, **36**, 1861 (1903); K. v. Auwers and W. Jülicher, *Ber.*, **55**, 2167 (1922), and earlier papers.

(2) R. L. Tse and M. S. Newman, *J. Org. Chem.*, **21**, 638 (1956).

(3) K. v. Auwers, *Ber.*, **44**, 588 (1911).

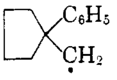
(4) C. Walling, *Free Radicals in Solution*, John Wiley and Sons, Inc., New York, 1957, Chap. 2; W. A. Roth, *Z. Elektrochem.*, **16**, 658 (1910).

The Effect of Incorporated Cycloalkyl Rings upon the Rearrangement of Neophyl-like Radicals

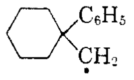
Sir:

The generation of carbon radicals in solution in order to study their possible rearrangement is perhaps best achieved by the di-*t*-butyl peroxide-induced decarbonylation of the appropriate aldehydes.[1]

Using this technique, we have investigated the rearrangement ability of some neophyl-like[2] radicals possessing incorporated cycloalkyl ring structures (I and II below).



I



II

The results indicate that the size of the ring present in such a radical affects its rearrangement ability appreciably. Little information on such a point seemed available heretofore.[3]

1-Phenylcyclopentylacetaldehyde (III, b.p. 106° at 1 mm., $n_D^{20.5}$ 1.5352, d_4^{20} 1.065, *Anal.*, Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.69; H, 8.37. 2,4-DNP m.p. 132–133°, *Anal.*, Calcd. for $C_{19}H_{20}N_4O_4$: N, 15.21. Found: N, 15.25) and 1-phenylcyclohexylacetaldehyde (IV, b.p. 112° at 0.5 mm., n_D^{20} 1.5395, d_4^{20} 1.080, *Anal.*, Calcd. for

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(1) Among others, S. Winstein and F. H. Seubold, Jr., *J. Am. Chem. Soc.*, **69**, 2916 (1947); W. H. Urry and N. Nicolaides, *J. Am. Chem. Soc.*, **74**, 5163 (1952); D. Y. Curtin and M. J. Hurwitz, *J. Am. Chem. Soc.*, **74**, 5381 (1952); and F. H. Seubold, Jr., *J. Am. Chem. Soc.*, **75**, 2532 (1953).

(2) The neophyl radical itself is $C_6H_5C(CH_3)_2CH_2$.

(3) M. A. Muhs, dissertation (University of Washington, 1954), quoted in H. Breederveld and E. C. Kooyman, *Rec. trav. chim.*, **76**, 305 (1957), has noted *no* rearrangement in radicals analogous to I and II with a methyl group in place of the phenyl group. Thus far alkyl groups have never been observed to rearrange in decarbonylation reactions.