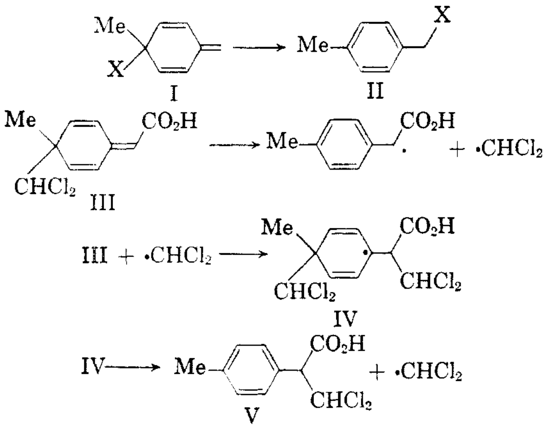
Communications TO THE EDITOR

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).

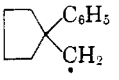
[4] C. Walling, *Free Radicals in Solution*, John Wiley and Sons, Inc., New York, 1957, Chap. 2; W. A. Roth, *Z. Elektrochem.*, **16**, 658 (1910).

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

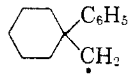
Sir:

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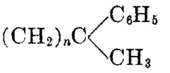
[1] Among others, S. Winstein and F. H. Seubold, Jr., *J. Am. Chem. Soc.*, **69**, 2916 (1947); W. H. Urry and N. Nicolaides, *J. Am. Chem. Soc.*, **74**, 5163 (1952); D. Y. Curtin and M. J. Hurwitz, *J. Am. Chem. Soc.*, **74**, 5381 (1952); and F. H. Seubold, Jr., *J. Am. Chem. Soc.*, **75**, 2532 (1953).

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

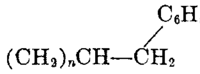
[3] M. A. Muhs, dissertation (University of Washington, 1954), quoted in H. Breederveld and E. C. Kooyman, *Rec. trav. chim.*, **76**, 305 (1957), has noted *no* rearrangement in radicals analogous to I and II with a methyl group in place of the phenyl group. Thus far alkyl groups have never been observed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

$C_{14}H_{18}O$: C, 83.14; H, 8.95. Found: C, 82.95; H, 9.09. 2,4-DNP m.p. 163–164°, *Anal.*, Calcd. for $C_{20}H_{22}N_4O_4$: N, 14.65. Found: N, 14.53) have been prepared[4] and decarbonylated with di-*t*-butyl peroxide (10–20 mole %) to mixtures of the hydrocarbons V and VI in yields of 64–74% ($n = 4$)



$(CH_2)_nC(C_6H_5)(CH_3)$

V



$(CH_2)_nCH{-}CH_2C_6H_5$

VI

$n = 4,5$

and 21–47% ($n = 5$). The conditions used and the rearrangement percentages obtained (infrared analysis by comparison with known mixtures of authentic V and VI) are shown in Table I.

TABLE I

Acetaldehyde	Rearrangement (%)[5] at Various Temperatures (Bath, °C) 140°[a]	190°[a]	132°[b]	160°[c]
1-Phenylcyclopentyl (III)	63	71	92	<3
1-Phenylcyclohexyl (IV)	89	91	94	50

[a] Pure aldehyde. [b] Aldehyde 1*M* in chlorobenzene. [c] Benzyl mercaptan (20 mole %) present.

The decarbonylation of β-phenylisovaleraldehyde to mixtures of iso- and *t*-butylbenzene has been previously reported to give the following rearrangement percentages: 57 (130°, 150°)[5,6]; 63 (170°)[5,6]; ~80 (130°, aldehyde 1*M* in chlorobenzene)[6]; and "the amount of rearrangement . . . decreases as benzyl mercaptan is added."[7] It is apparent from Table I that the cyclopentyl ring in I is somewhat comparable to the *gem*-dimethyl function in the neophyl radical[2] in its effect upon this radical rearrangement, while the cyclohexyl ring in II increases the amount of rearrangement significantly.

At some initial aldehyde concentration, two factors determine the amount of rearrangement of a neophyl-like radical: the *half-life* of the radical (a measure of its stability); and the *chain transfer ability* of the parent aldehyde (a measure of the ease of aldehydic hydrogen atom abstraction by chain-carrying radicals). Scale models[8] of the radicals I and II indicate that serious steric hindrance to benzene ring rotation about the cycloalkyl ring-phenyl bond is present in the cyclopentyl case and absent in the cyclohexyl case. Such additional rotational freedom in II should increase its half-life (stability) relative to I and thereby allow II more time to rearrange. This restricted rotation in I hinders maximum overlap of the carbinyl carbon *p* (or sp^3) orbital (possessing the unpaired electron) with the π-molecular orbital of the benzene ring. Since such overlap is considered to be a prerequisite for the ready migration of the phenyl group,[9] this hindrance should slow the rearrangement process in the cyclopentyl instance.[10] On the other hand, qualitative rate data show that under comparable conditions III is decarbonylated two to four times faster than is IV and to an extent nearly twice that of IV. Such data can be accommodated if III has the more easily abstracted aldehydic hydrogen atom (greater chain transfer ability).[11] Confirmation of this point may be found in the apparently greater chain length process with III. Here 10 mole % of di-*t*-butyl peroxide suffices for nearly complete decarbonylation, while 20 mole % peroxide is needed for half-complete decarbonylation in IV.

These results will be presented soon in detail. The rearrangement ability of neophyl-like radicals with other incorporated cycloalkyl rings is also under investigation in this laboratory.

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[4] The appropriate 2-phenylcycloalkanone was substituted at C-2 with allyl chloride using sodium amide. Huang-Minlon reduction to the hydrocarbon, followed by performic acid hydroxylation of the allylic double bond and subsequent cleavage of the vic-glycol with lead tetraacetate afforded the appropriate aldehyde.

[5] The results are ±3%.

[6] F. H. Seubold, Jr., *loc. cit.*

[7] S. Lapporte, unpublished work mentioned by S. Winstein *et al.*, *Experientia*, **12**, 138 (1956).

[8] Fisher-Taylor-Hirschfelder models were used with the carbinyl carbon (radical) portion *either* trigonal planar (sp^2) *or* tetrahedral (sp^3), and, in II, with the phenyl group equatorial on a chair-form cyclohexane ring.

[9] J. Hine, *Physical Organic Chemistry*, McGraw-Hill Book Co., New York, N. Y., 1956, p. 448.

[10] A referee has suggested that II may be *bridged*, thereby allowing relief from the steric strain due to the axial —$CH_2\cdot$, and accommodating the apparent insensitivity of the rearrangement to concentration. While extensive discussion will properly be reserved until later, we feel that the decreased rearrangement in the presence of mercaptan argues against such a bridged structure.

[11] Concerning this point, the above referee has pointed out that the axial conformation of the —CH_2CHO in IV renders its aldehydic hydrogen relatively inaccessible.