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Rearrangements of Halomagnesium Derivatives of Halohydrins

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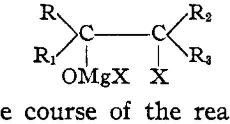
The rearrangement, by heating, of the halomagnesium derivatives of *cis*-2-chloro-1-indanol and *cis*-2-chloro-1-methyl-1-indanol, results in the smooth formation of 1-indanone and 2-methyl-1-indanone, respectively. The corresponding *trans* compounds give the same ketones in very low yields, along with large amounts of tarry and polymeric materials. The significance of these results to the question of the rearrangements of 1,2-halohydrins is discussed from the standpoint of two mechanisms for reactions of this kind.

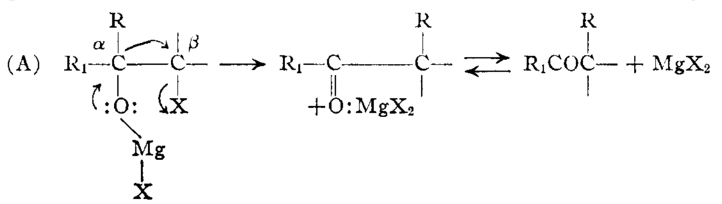
Halomagnesium derivatives of halohydrins are the first products of the normal reaction[1] of Grignard reagents with α-halocarbonyl compounds. They may, under appropriate conditions, react further to yield products which appear to have arisen from a secondary reaction of the reagent with an oxide or carbonyl compound derived from the halohydrin. Reactions of this kind have been investigated in detail by Tiffeneau and his students,[2] who have elucidated the main features of the transformations which are involved.

Although Tiffeneau has recognized the importance of the stereochemical arrangement of the groups attached to the essential structural element (I) in directing the course of the rearrangements, he has discussed these important details in terms which explicitly invoke neither the stereochemical concepts upon which our present-day understanding of molecular rearrangements is based, nor the characteristic properties of the (electrophilic) magnesium atom and the (nucleophilic) halogen atom involved in these reactions.



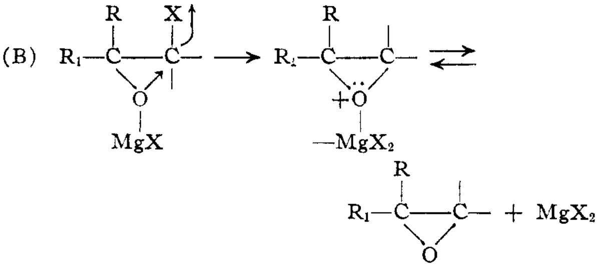
(I)

An extensive review of the voluminous literature on this subject cannot be given here, but certain facts pertinent to the present discussion require review. The majority of the rearrangements of halomagnesium derivatives of halohydrins can be accounted for by considering them to be pinacol-like rearrangements induced by an electrophilic attack of the –MgX grouping upon the neighboring halogen atom (A)



II III IV

A second way in which II may react, and a course which seems to be followed in a limited number of cases, is by a displacement of the β-halogen atom by a nucleophilic attack of the oxygen atom upon the carbon atom to which X is attached. It is probable that a "solvation" of the departing halogen atom by some external electrophile is involved in this step (B)



Whether mechanism A or B is followed in the rearrangement of II will be determined by structural factors. Course A should be favored when the halogen atom is secondary or tertiary rather than primary; when the migrating R group can participate in the process and contribute to the resonance stabilization of the transition state; and when the relative disposition of –X and –OMgX is *cis*. Course B should be favored when –X and –OMgX are *trans*; or, if these are or can be *cis*, when the halogen atom is primary and the migrating R group has a low migratory aptitude (*i.e.*, contributes little to resonance stabilization of the transition state).

When the halogen atom is secondary or tertiary, course A seems always to be followed; but when it is primary the nature of groups R and R_1 directs the course of the rearrangement, as illustrated by the examples (C)[3] and (D)[4].

In reaction (C), to which the "oxide" mechanism (B) applied, the electrophilic withdrawal of the primary β-chlorine atom is not sufficiently aided by participation of the neighboring alkyl groups (R or methyl) to allow a rearrangement according to (A) to occur, and the ready displaceability of the halogen by a nucleophilic attack of oxygen on carbon takes precedence. In (D), however, which appears to proceed by the "withdrawal" mechanism (A), the ability of the phenyl group to participate effectively in and thus to afford added stabilization to the transition state involved in its migration, favors the rearrangement to phenylacetone. It should be noted that the oxide which would be formed in (D) by way of mechanism (B) would rearrange to hydratropaldehyde and not to phenylacetone.[4,5]

The influence of stereochemical factors is illustrated by the rearrangements of *cis* and *trans* halo-

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[1] The non-addition reactions of α-haloketones and Grignard reagents, which result in the formation of halomagnesium enolates with the elimination of RH or RX (R from RMgX), are not included in this discussion.

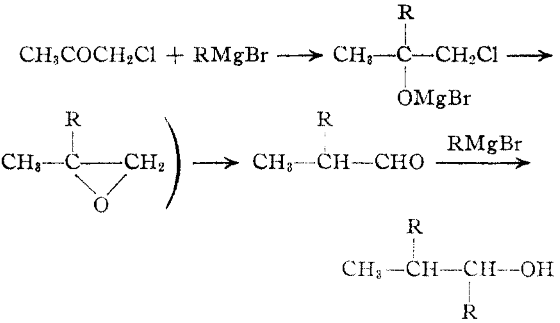
[2] For a review, see M. Tiffeneau, *Bull. soc. chim.*, [5] **12**, 621 (1945).

[3] M. Tiffeneau, *Compt. rend.*, **137**, 989 (1903); L. Henry, *ibid.*, **145**, 21 (1907); E. Fourneau and M. Tiffeneau, *ibid.*, **145**, 437 (1907); L. P. Kyriakides, THIS JOURNAL, **36**, 657 (1194); R. C. Huston, R. I. Jackson and G. B. Spero, *ibid.*, **63**, 1459 (1941).

[4] M. Tiffeneau, *Compt. rend.*, **140**, 1458 (1905).

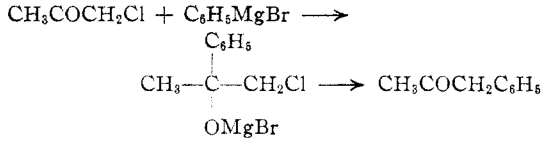
[5] S. Danilow and E. Venus-Danilowa, *Ber.*, **60B**, 1050 (1927)

(C)



R = CH_3, C_2H_5, i-C_5H_{11}, $CH_2C_6H_5$.

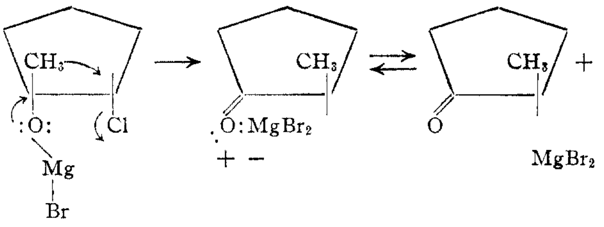
(D)



$CH_3COCH_2Cl + C_6H_5MgBr \longrightarrow CH_3\overset{C_6H_5}{\underset{OMgBr}{C}}CH_2Cl \longrightarrow CH_3COCH_2C_6H_5$

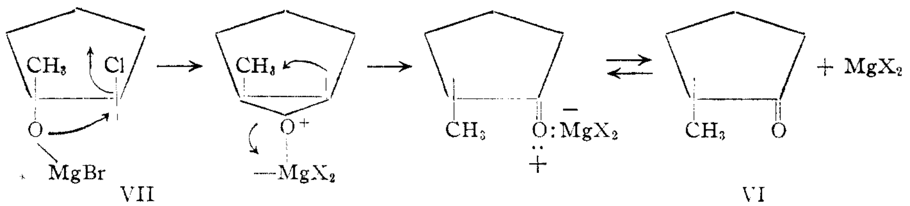
hydrins in the cyclohexane series. Tiffeneau and Tchoubar[6] observed that the rearrangement, *via* the halomagnesium derivative, of *cis*-1-methyl-2-chlorocyclohexanol yielded mostly 2-methylcyclohexanone and a small amount of acetylcyclopentane, while the rearrangement of the *trans* isomer afforded acetylcyclopentane only. It is apparent from an examination of molecular models that the migrating groups (the ring bond in the *trans* case, the methyl group in the *cis*) are so disposed as to be able to displace the departing halogen atom by a rearward attack, and thus presumably by a Walden inversion. Because of the non-planar nature of the cyclohexane ring, both the *cis* and the *trans* halohydrins can assume the configuration requisite to rearrangement by the "withdrawal" mechanism (A). That rearrangement by the "oxide" mechanism (B) does not occur in the case of the *trans* isomer is shown by the observation that *trans*-1,4-dimethyl-2-chlorocyclohexanol rearranges to yield 3-methyl-1-acetylcyclohexane and no other product.[6,7] A reexamination of the latter reaction in this Laboratory[8] has confirmed this finding; a careful search failed to disclose the presence of either 1,3-dimethylcyclopentylformaldehyde or 2,5-dimethylcyclohexanone, the products to be expected from the rearrangement of 1,2-epoxy-1,4-dimethylcyclohexane.

In view of the above considerations it was of interest to find that Tiffeneau and Vaissière[9] reported that the rearrangement of the halohydrin derivatives of both *cis*- (V) and *trans*-1-methyl-2-chlorocyclopentanol (VII) led to the same compound, namely, 2-methylcyclopentanone (VI), and that they stated that "there is no difference in behavior between the *cis*- and *trans*-derivatives."[10] The formation of 2-methylcyclopentanone from *cis*-1-methyl-2-chlorocyclopentanol can be accounted for readily by assuming the rearrangement to occur by the "withdrawal" mechanism (A)



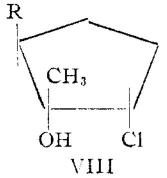
V VI

The rearrangement of the *trans* isomer cannot be represented by a "withdrawal" mechanism since (a) the magnesium and chlorine atoms are widely separated, and (b) the removal of the chlorine atom by an intermolecular attack (of some electrophilic agent in the solution) would be a process to which no assistance could be tendered by the participation of an adjacent group in the course of migration to the resulting cationoid carbon atom in a concerted process. It therefore appeared that Tiffeneau and Vaissière's result might be accounted for by the "oxide" mechanism (B)

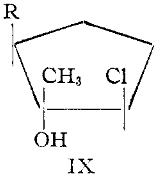


VII VI

It is evident that if this were the case, the cyclopentanones derived from an appropriately substituted pair of halohydrins, VIII and IX

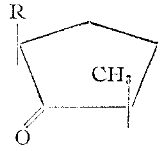


VIII

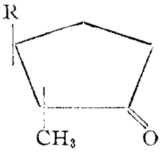


IX

would be the structurally isomeric compounds X and XI



X



XI

In order to examine this hypothesis, the present study was carried out with the use of indane derivatives in order to avoid the obvious difficulties which would be involved in the use of compounds such as VIII–XI. It was anticipated that *cis*-2-halo-1-indanols would give 1-indanone by the "withdrawal" mechanism (A), and, if the *trans*-isomers rearranged by way of the oxide, 2-indanone would be formed. Indene oxide has been shown to yield 2-indanone when subjected to rearrangement by

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(6) M. Tiffeneau and B. Tchoubar, *Compt. rend.*, **199**, 360 (1934).

(7) In a later paper, M. Tiffeneau, B. Tchoubar and S. LeTellier, *ibid.*, **216**, 856 (1943), have reported that carefully purified *cis*-1,4-dimethyl-2-chlorocyclohexanol gives only 2,4-dimethylcyclohexanone.

(8) R. I. Akawie, M.S. Thesis, U. C. L. A., 1943, to be published.

(9) M. Tiffeneau and G. Vaissière, *Compt. rend.*, **209**, 449 (1939).

(10) It is not clear, of course, from this statement whether the "behavior" of the compounds was regarded in terms of the products isolated or in terms of the mechanism of the rearrangement.

heating with infusorial earth,[11] treatment with magnesium bromide[11] or zinc chloride[12] in ether, and by refluxing with dilute sulfuric acid.[12]

Tchoubar[11] has reported that *trans*-2-bromo-1-indanol, when subjected to rearrangement by heating its bromomagnesium derivative, was transformed into 1-indanone. She reported no yield and characterized the product of the reaction by means of its melting point (41°) and that of its semicarbazone (247°). Since other reported melting points for the semicarbazone (233°,[13] 239° (dec.)[14]) differed so markedly from this as to cast doubt upon the validity of an identification based upon this derivative, it was necessary to reexamine the rearrangment of *trans*-2-bromo-1-indanol.

The characterization of 1- and 2-indanone was studied by the preparation of the pure ketones and four derivatives of each. The *p*-nitrophenylhydrazones, oximes and semicarbazones were rejected as suitable derivatives because of insufficient differences in melting or decomposition points, and the 2,4-dinitrophenylhydrazones (DNPH) chosen because of their widely differing melting points (1-indanone: m.p. 257–257.5° (dec.)[15,16]; 2-indanone, m.p. 198–199° (dec.)[17]), and the marked color difference which is characteristic of the DNPH derivatives of aryl (orange to red) and alkyl (yellow) ketones.

trans-2-Bromo-1-indanol was converted into the iodomagnesium derivative by treatment with ethylmagnesium iodide. After the ethereal suspension of the resulting white solid had been refluxed for ninety minutes with no appreciable change (unchanged bromohydrin was recoverable after hydrolysis), the ether was removed and replaced by dibutyl ether and the resulting mixture refluxed (temperature 114°, rising to 127°) for forty-two hours. After careful decomposition[18] of the dark, tarry reaction mixture with ammonium chloride solution there was isolated a polymeric brown solid, a tarry, steam-involatile material, and, in about 8% yield, 1-indanone. The infusible, brown solid was separated by Soxhlet extraction with ethanol into an alcohol-soluble tar and a dark-brown, insoluble solid material. The latter substance contained magnesium and halogen and gave analytical figures for carbon (50.1%) and hydrogen (5.1%) which were intermediate between those calculated for a polymeric indanone $(C_9H_8O)_n$ and a polymeric halomagnesium salt of an indenol $(C_9H_7OMgBr)_n$, but closer to the latter. Oxidation of the polymer with potassium permanganate afforded phthalic acid, suggesting that the indane skeleton is present in the material.

In another experiment the bromomagnesium derivative of *trans*-2-bromo-1-indanol was heated in benzene, 25-ml. samples being withdrawn after 2.5, 5, 8, 12 and 23.5 hours of refluxing. The amount of indanone in each aliquot was estimated by conversion of the ketonic products into the 2,4-dinitrophenylhydrazones. The results are given in Table I.

TABLE I

42.6 g. (0.20 mole) of *trans*-2-bromo-1-indanol, 0.20 mole of *n*-butylmagnesium bromide, 500 ml. of benzene, 80°.

Sample	Elapsed time, hr.	Color of dvt.	M.p.,[a] °C.	Yield of dvt., g.[b]
1	2.5	Maroon	244–247	0.2
2	5	Copper-red	244–247	.4
3	8	Brown-red	245–248	.5
4	12	Brown-red	246–248	.6
5	23.5	Bright red	251–254	.2
(1-indanone	..	Bright red	254–255	...)

[a] Without recrystallization. [b] From a 25-ml. aliquot of the original reaction mixture.

These results dispose of the probability that the low yield of 1-indanone obtained in the first experiment was the result of its destruction during the heating period, since the maximum yield of (impure) derivative obtained after twelve hours represented at the most a 20% yield of the ketone. Moreover, the change in color and the rise in the melting point of the derivative as the reaction progressed suggested that in the early stages of the reaction a small amount of another ketonic material (2-indanone ?) was present, which disappeared as the reaction was allowed to proceed.

Thus it appears that, as Tchoubar reported, 1-indanone is indeed the product of the rearrangement of the *trans*-bromohydrin, but it was produced only as a minor product in a reaction which appeared to take predominantly another course.

Attempts to prepare *cis*-2-bromo-1-indanol by a variety of methods were unsuccessful. Read and Hurst[19] reported the isolation of a substance isomeric with *trans*-2-bromo-1-indanol, possibly the *cis* isomer, but our efforts to obtain this substance by their procedure were fruitless. Attention was then turned to the *cis*- and *trans*-2-chloro-1-indanols and -2-chloro-1-methyl-1-indanols. *cis*- and *trans*-2-chloro-1-indanols were prepared by the method of Suter and Lutz.[15] The structures of these compounds, both crystalline solids, have been established by unambiguous methods.[20] The *cis*-chlorohydrin was converted into the bromomagnesium derivative by means of *n*-butylmagnesium bromide, and after removal of the ether the dry solid was heated on the steam-bath (95°) for six hours. The initially white solid became brown and turned dry and powdery. After hydrolysis with ammonium chloride solution 1-indanone was isolated as the DNPH. The yield of 1-indanone was 71%. In a second experiment the bromomagnesium derivative of the *cis*-chlorohydrin was heated in boiling dibutyl ether for forty hours; the yield of 1-indanone was 69%. In both of these experiments the amount of tarry or polymeric material formed was very small, the second run offering additional evidence that long-continued heating at the boiling-point of dibutyl ether results in little destruction of the 1-indanone by the action of magnesium salts present in the solution.

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[11] B. Tchoubar, *Compt. rend.*, **214**, 117 (1942).

[12] J. Böeseken and C. van Loon, *Proc. Acad. Sci. Amsterdam*, **20**, 1186 (1918); *C. A.*, **13**, 314 (1919).

[13] K. von Auwers and E. Auffenberg, *Ber.*, **52B**, 92 (1919).

[14] C. Revis and F. S. Kipping, *J. Chem. Soc.*, **71**, 238 (1897).

[15] C. M. Suter and G. A. Lutz, THIS JOURNAL, **60**, 1360 (1938).

[16] C. F. H. Allen, *ibid.*, **52**, 2955 (1930).

[17] C. M. Suter and H. B. Milne, *ibid.*, **62**, 3473 (1940).

[18] H. D. Porter and C. M. Suter, *ibid.*, **57**, 2022 (1935), found that the *trans*-bromohydrin is converted to 1-indanone by heating with acid.

[19] J. Read and E. Hurst, *J. Chem. Soc.*, **121**, 2550 (1922).

[20] C. Courtot, Fayet and Parant, *Compt. rend.*, **186**, 371 (1928).

When the *trans*-chlorohydrin was rearranged (as the bromomagnesium derivative) by heating in boiling dibutyl ether for forty hours, the results were strikingly similar to those obtained in the case of the *trans*-bromohydrin. The major products of the reaction were tarry and polymeric materials, 1-indanone being isolated (as the DNPH) in 7% yield.

A study of the behavior of *cis*- and *trans*-1-methyl-2-chloro-1-indanol disclosed that the rearrangements of the bromomagnesium derivatives of these isomers followed courses similar to those observed in the case of the preceding pair of *cis*- and *trans*-chlorohydrins. The *cis* isomer rearranged smoothly to yield 64–79% of 2-methyl-1-indanone, while the *trans* isomer yielded mostly tarry materials along with 5% of the same ketone.

The preparation of the 1-methyl-2-chloro-1-indanols and of the bromomagnesium derivative of the *trans* compound offer some features of interest. *cis*-1-Methyl-2-chloro-1-indanol was prepared by the method used for the preparation of certain other cyclic halohydrins by Bartlett and Rosenwald.[21] The yield of product giving satisfactory analytical figures (chlorine) for the desired chlorohydrin was 73%, and analysis of this material for its content of *trans* isomer by titration with alkali[15] showed that it was a mixture of 93% of the *cis* and 7% of the *trans* chlorohydrins.

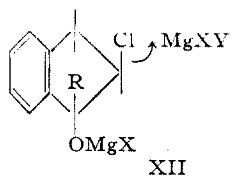
trans-1-Methyl-2-chloro-1-indanol was more difficult to prepare. The addition of hypochlorous acid to 3-methylindene proved unsatisfactory at first, and it was found that the reaction of N-chloroacetamide[22] with 3-methylindene, at room temperature for six days in a slightly acid medium, afforded a 37% yield of a chlorohydrin which gave good analytical figures (chlorine) for the expected compound. However, when it was found that the rearrangement of this material, as the bromomagnesium derivative, resulted in an unexpectedly high yield (57%) of 2-methyl-1-indanone, the starting material was examined with more care. Analysis by titration with alkali showed that the supposedly *trans* compound was actually a mixture containing about 73% of the *cis* isomer. It is probable that the addition of the elements of hypochlorous acid to the indene produced the *trans*-chlorohydrin and that the prolonged contact with the acidic reaction medium brought about the rearrangement to the *cis* isomer. Similar isomerizations of glycols and halohydrins[17] are not uncommon; and it is suggested that in the present example the *cis* form possesses the more stable configuration as a result of hydrogen bonding between the hydroxyl hydrogen atom and the neighboring chlorine atom.

The method finally adopted for securing the halomagnesium derivative of *trans*-1-methyl-2-chloro-1-indanol consisted in the addition during two and one-half hours of hypochlorous acid to 3-methylindene in nearly neutral solution. The crude chlorohydrin was purified superficially only and treated, in ether, with an ether solution of *t*-butylmagnesium chloride. The resulting precipitate was separated from the solution and washed thoroughly with ether; it represented about 34% of the original (crude) chlorohydrin, which probably contained 1-methyl-1,2-dichloroindene and unchanged 3-methylindene, both of which would be removed by the washing of the chloromagnesium derivative. Since a titration of the crude chlorohydrin-containing mixture showed a rapid initial consumption of alkali corresponding to 35–40% of the *trans* compound, the amount of chloromagnesium derivative corresponded well with what was expected.

The 2-methyl-1-indanone formed in the experiments with the 1-methyl-2-chloro-1-indanols was estimated by converting it to the 2,4-dinitrophenylhydrazone, an authentic sample of which was prepared from 2-methyl-1-indanone prepared by the method of Fuson, Ross and McKeever.[23]

Discussion.—The smooth rearrangements of *cis*-2-chloro-1-indanol and *cis*-1-methyl-2-chloro-1-indanol to the respective 1-indanones is readily interpreted in terms of the pinacol-like rearrangement represented in mechanism A. The strikingly different behavior of the corresponding *trans* compounds, with the formation of the same ketones very low yields and large amounts of tarry and polymeric substances, suggests that when the smooth and concerted process A cannot occur because of steric reasons, more complex reactions result. The results with the *trans* compounds do not support the supposition that in these cases the "oxide" mechanism obtains, but they do not dispose of this explanation since the 2-indanone which would result from such a process would undoubtedly fail to survive under the conditions of the reaction in the presence of magnesium halides in the solution. The considerable reactivity of the 3-methylene group in the 2-indanones because of its proximity to the aromatic ring and to a carbonyl group is a point of difference between the case examined by Tiffeneau and Vaissière and the present work. A cyclopentanone would be more likely to survive than a 2-indanone, being in this respect comparable to the 1-indanones, which are not destroyed under the rather vigorous conditions used in carrying out the rearrangements.

The presence of the 1-indanones among the products of the rearrangement of the *trans*-halohydrins could be the result of a side-reaction accompanying the main reaction, if the latter takes the "oxide" course. However, the 1-indanones could result as products of a reaction, leading chiefly to polymers, which does not go through an oxide, but proceeds through an electrophilic removal of the halogen atom by an intermolecular attack (XII) of some species of –MgX compound in the solution



XII

The loss of steric identity of the resulting carbonium ion, allowing the shift of R to the 2-position, would yield the 1-indanone. The loss of a proton from the

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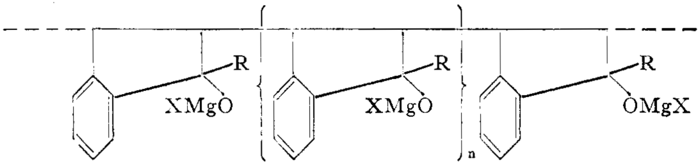
[21] P. D. Bartlett and R. H. Rosenwald, THIS JOURNAL, **56**, 1990 (1934).

[22] Compare E. Schmidt, W. von Knilling and A. Ascherl, *Ber.*, **59B**, 1279 (1926).

[23] R. C. Fuson, W. E. Ross and C. H. McKeever, THIS JOURNAL, **60**, 2935 (1938).

3-position, by a process simulating a first-order elimination reaction, would lead to the halomagnesium derivative of a 1-indenol, the polymerization of which through the agency of the 2-carbonium ion derived from XII would account for the formation of a polymer, the simplest structure for which would be XIII



XIII

It would, however, be difficult to understand the formation from XII of a carbonium ion in an appreciable concentration in view of the availability of the nucleophilic oxygen atom so favorably disposed to participate in the process of halogen removal. It appears most likely that the "oxide" mechanism obtains, the 1-indanones being formed as the result of the action of the halogen atom of the –OMgX group as a rearward displacing agent during the process of electrophilic withdrawal of the 2-halogen atom depicted in XII—a side-reaction which must occur to a relatively minor extent only. The polymerization of the resulting 2-indanones by magnesium salts could account for the formation of the polymers observed.

Experimental[24]

trans-**2-Bromo-1-indanol** was prepared by the method of Suter and Milne.[17] Yields of 90–98% of crude material, m.p. 126°, were obtained. After recrystallization from ethanol the bromohydrin melted at 129.8–130.2° (literature,[25] 128–129°).

1-Indanone[18] and **2-indanone**[26] were prepared by known methods.

Rearrangement of *trans*-**2-Bromo-1-indanol.**—(A) To a solution of 42.6 g. of *trans*-2-bromo-1-indanol in 800 ml. of dry ether was added, dropwise and with stirring, 244 ml. of 8 molar ethereal ethylmagnesium iodide. Gas was evolved steadily and a white precipitate formed. The mixture was refluxed for an hour after addition was completed.[27] The ether was removed by distillation, leaving a white solid. To this was added 500 ml. of freshly distilled dibutyl ether and the mixture was refluxed for 42 hours. The white suspension soon darkened and then thickened and became so tarry as to make stirring impossible. The temperature of the mixture rose from an initial 114° to a final 127°. The mixture was cooled and hydrolyzed with cold ammonium chloride solution, the brittle tar being broken from the sides of the flask and separated on a filter.

The dibutyl ether solution was separated from the filtrate, dried and distilled through a Vigreux column. The material which did not distill at the temperature of the steam-bath and at 20–25 mm. (water pump) was a tarry liquid (12.3 g.). This was subjected to steam distillation, yielding 2.3 g. of a steam-volatile, yellow oil. This was shown to be 1-indanone by the preparation of the 2,4-dinitrophenylhydrazone, m.p. 254–255° (dec.). The steam-involatile material was a black, tarry substance (9.6 g.).

The solid material separated in the first filtration (18.0 g.) was extracted (Soxhlet) with ether for three hours. Evaporation of the extract left a black tar (7.5 g.) containing a small quantity of white crystalline material. This could be extracted with ethanol and recrystallized from the same solvent. The recrystallized material did not melt below 430°, and when subjected to analysis proved to contain no carbon. The ether-insoluble solid (11.5 g.) was dark brown, and when burned left an ash which contained magnesium. A sodium fusion test showed the presence of halogen.

Anal. Found: C, 50.10; H, 5.11.

The polymer was oxidized with alkaline potassium permanganate solution.[28] After sixteen hours of refluxing the polymer had been only partially attacked. Extraction of the acidified filtrate with ether and removal of the ether gave a solid which was sublimed at atmospheric pressure. The colorless sublimate melted at 129–130.5°, and when mixed with phthalic anhydride, at 130–131°.

(B).—The bromomagnesium derivative (prepared by the addition of butylmagnesium bromide) was prepared in the manner described in (A). The ether was removed and replaced with 500 ml. of benzene, and the resulting mixture heated to boiling under reflux. The solid dissolved and the solution slowly darkened. Twenty-five-ml. samples were withdrawn after 2.5, 5, 8, 12 and 23.5 hours. Each sample was diluted with benzene and washed with cold 1 *N* hydrochloric acid, water, saturated sodium bicarbonate solution and again with water. The benzene solution was evaporated and to the residue was added a hot solution of 0.375 g. of 2,4-dinitrophenylhydrazine and 0.75 ml. of concentrated hydrochloric acid in 25 ml. of ethanol. The solution was refluxed briefly, cooled, and the precipitate collected and washed with ethanol. The results are given in Table I.

cis- **and** *trans*-**2-Chloro-1-indanol.**—These were prepared from 1,2-dichloroindane by the method of Suter and Lutz.[15] The *trans*-chlorohydrin, obtained in 35% yield, melted at 125.2–125.7° (literature,[20] 126°). The *cis*-isomer, obtained in 3.4% yield, melted at 110–110.5° (literature,[20] 110–111°).

Rearrangement of *cis*-**2-Chloro-1-indanol.**—(A) The preparation of an ether suspension of the bromomagnesium derivative of 8.4 g. of the chlorohydrin was carried out as described above for the bromohydrin. The ether was removed and the white solid remaining was heated on the steam-bath for six hours. The solid turned brown and became dry and powdery. After hydrolysis with ammonium chloride ether was added and the organic layer removed. Evaporation of the ether left 5.9 g. of an oil, which was transferred to a volumetric flask and made up to 100 ml. with ethanol. An aliquot portion of 10 ml. of this solution yielded 1.105 g. of the 2,4-dinitrophenylhydrazone of the 1-indanone, m.p. 258.5–259°. The total yield of 1-indanone was therefore 71% of the theoretical.

(B).—The rearrangement of the bromomagnesium derivative of 8.0 g. of the *cis*-chlorohydrin was carried out in boiling dibutyl ether (40.5 hours). The cooled reaction mixture was treated with ammonium chloride solution, the dibutyl ether layer separated and the solvent removed. The residual oil (4.4 g.) was converted into the DNPH as described in (A). A 10-ml. aliquot yielded 1.025 g. of the derivative; this corresponds to a 69% yield of 1-indanone.

Rearrangement of *trans*-**2-Chloro-1-indanol.**—The rearrangement of the bromomagnesium derivative of 33.7 g. of the *trans*-chlorohydrin in dibutyl ether (39.5 hours), and the isolation of the products, were carried out in the manner described above for the *trans*-bromohydrin. The yields of the various fractions were as follows: 1-indanone, 7.3% (4.1 g. of the crude material, converted into the DNPH); tarry (liquid) material, 9.9 g.; ether-insoluble brown polymer, 9.7 g.

cis-**1-Methyl-2-chloro-1-indanol.**—The addition of 140 ml. of 2.34 molar ethereal methylmagnesium bromide to a benzene solution (500 ml.) of 53.8 g. of 2-chloro-1-indanone[20] was carried out with cooling of the reaction mixture in ice, followed by stirring for an hour at room temperature. After decomposition of the mixture with ammonium chloride solution the organic layer was separated, the solvent removed, and the residue distilled. After a forerun of 1 ml. the material distilled at 85–86° at 1.5 mm. The yield was 43.1 g. (73%) of a colorless liquid, $n^{25.5}\text{D}$ 1.5592.

Anal. Calcd. for $C_{10}H_{11}OCl$: Cl, 19.41. Found: Cl, 19.69.

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[24] Melting points, but not boiling points, are corrected.

[25] W. J. Pope and J. Read, *J. Chem. Soc.*, **99**, 2071 (1911).

[26] L. S. Walters, *J. Soc. Chem. Ind.*, **46**, 150 T (1927).

[27] In a separate experiment, hydrolysis of the mixture at this point resulted in the recovery of bromohydrin.

[28] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," third edition, John Wiley and Sons, New York 1, N. Y., 1948, p. 198.

The product was analyzed for its content of the *trans* isomer by the method of Suter and Lutz.[15] To a solution of 0.4334 g. of the compound in 100 ml. of boiling water containing three drops of phenolphthalein indicator was added, with stirring, 0.1140 *N* sodium hydroxide at a rate sufficient to keep the solution faintly pink. The following data were taken:

Time (min.)	Vol. of base	% Reaction
0:50	0.99	4.76
2:00	1.46	7.01
5:00	1.58	7.95
49:00	2.16	10.37

The product contained about 7% of the *trans* isomer.

Rearrangement of *cis*-1-Methyl-2-chloro-1-indanol.—The rearrangement of the bromomagnesium derivative of the *cis*-chlorohydrin was carried out in the absence of solvent as described for the case (A) of *cis*-2-chloro-1-indanol. A yield of 64% of 2-methyl-1-indanone (DNPH, m.p. 221–222°) was obtained.

2-Methyl-1-indanone was prepared by the method of Fuson, Ross and McKeever.[23] The 2,4-dinitrophenylhydrazone, prepared by the usual method, formed crimson crystals, m.p. 221.5–222° (from benzene).

Anal. Calcd. for $C_{16}H_{14}N_4O_4$: C, 58.89; H, 4.33. Found: C, 58.95; H, 4.57.

Preparation and Rearrangement of *trans*-1-Methyl-2-chloro-1-indanol.—(A) The chlorohydrin prepared by shaking for six days an aqueous solution of N-chloroacetamide, containing a few drops of sulfuric acid, with 3-methylindene was converted into the bromomagnesium derivative and the latter heated for three hours at 100°. The reaction mixture was worked up as usual, affording a 58% yield (based on the analytically satisfactory chlorohydrin) of 2-methyl-1-indanone. Analysis of the starting material by the titration procedure[15] disclosed that the chlorohydrin consisted of about 73% of the *cis* isomer. The yield of the indanone thus corresponds to 79% of the *cis* chlorohydrin used.

(B).—A sodium hypochlorite solution was prepared by passing chlorine into a mixture of 4.1 g. of mercuric chloride and 31.7 g. sodium hydroxide in 300 g. of a mixture of crushed ice and water.[29] The resulting solution was found to be 1.23 molar in sodium hypochlorite. To 312 ml. of this solution was added a solution of 24.0 ml. of 16 *N* nitric acid in 225 ml. of water and 1 g. of sodium bicarbonate.

To a stirred mixture of 18.2 g. of 3-methylindene and 50 g. of ice was added 250 ml. of the hypochlorous acid solution (0.64 *M*) in portions of 100, 100, 25 and 25 ml., the total time required being 2.5 hours. The organic phase was taken up in ether and the ether solution washed with water (twice), 3 *N* sodium carbonate (once) and water (once). Removal of the ether after drying over magnesium sulfate left 23.3 g. of an oil.

Anal. Calcd. for $C_{10}H_{11}OCl$: Cl, 19.41. Calcd. for $C_{10}H_{10}Cl_2$: Cl, 35.31. Found: Cl, 22.39.

Titration of a sample with alkali as described above gave the following data:

Time, min.	1.0	3.5	5.0	15.0
Reaction, %	28.8	39.1	44.5	51.2

These data show that the material contains less than 50% of the *trans* isomer, and probably about 35–40%. Because of the probable presence of some 1,2-dichloroindene the usual well-defined shoulder in the titration–time curve is absent, although the characteristic rapid initial reaction is clearly discernible.

(C).—**Rearrangement.**—After the addition of 81.6 ml. of 1.47 molar ethereal *t*-butylmagnesium chloride to a solution of 21.9 g. of the crude chlorohydrin, from (B), in 360 ml. of ether, the mixture was refluxed for an hour and the solvent removed through a sintered glass filter stick. The residue was washed with 100 ml. of ether, which was removed in the same way. The light brown solid residue (11.6 g., corresponding to 7.42 g. of chlorohydrin, or 34% of the crude material used) was heated at 100° for six hours. After hydrolysis and separation of the ethanol-soluble material from the black tarry substance which formed the bulk of the product, 0.75 g. of 2,4-dinitrophenylhydrazine and 1.5 ml. of concentrated hydrochloric acid were added to the ethanol solution (50 ml.). The red crystals of the DNPH of 2-methyl-1-indanone, which separated on standing, weighed 600 mg. This corresponds to a 4.5% yield of the ketone.

In another experiment the bromomagnesium derivative was prepared in the manner described above (C) and heated for forty hours in boiling dibutyl ether. The yield of DNPH of 2-methyl-1-indanone, m.p. and mixed m.p. 221–222°, corresponded to a 3% yield of the ketone.

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[29] G. H. Coleman and H. F. Johnstone, "Org. Syn.," Coll. Vol. I, 2nd ed., John Wiley and Sons, New York 1, N. Y., 1941, p. 158.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Studies in Photochemistry and Radiation Chemistry of *i*-Propylbenzene and *t*-Butylbenzene[1,2]

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Data on vapor phase photolyses of *i*-propylbenzene and *t*-butylbenzene with light of wave length near 2537 Å. are interpreted in terms of methyl radical production by a primary splitting of carbon-to-carbon bonds β to the benzene ring and hydrogen production principally via rupture of carbon-to-hydrogen bonds β and γ to the benzene ring. Liquid phase photolyses show almost complete suppression of hydrocarbon formation with total quantum yields of non-condensable gas 2.4×10^{-4} and 1.3×10^{-4}, respectively. Data for gas phase photolyses are sufficiently accurate only for the statement that the quantum yields are roughly of the same order of magnitude. Data on liquid-phase irradiations of these compounds with 1.5 Mev. electrons indicate that processes characteristic of excitation in the π-electron system make a relatively greater contribution to the over-all radiolytic effect than was apparent in previously reported data on toluene, mesitylene and ethylbenzene.

Introduction

Studies in the photochemistry of toluene, mesitylene and ethylbenzene[4] have shown that excitation in the π-electron system with light of wave length near 2537 Å. results in dissociation chiefly in bonds β to the benzene ring. In the case of ethylbenzene vapor, resultant ultimate products consist mostly of methane and ethane with but small amounts of hydrogen. Data on electron irradiation of these compounds in the liquid state[4] indicated that the observed radiolytic effects might be mainly the result of primary physical effects in the side group plus a contribution from processes ensuant on excitation in the π-system such as are observed in the vapor state photolyses.

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(2) Abstract from a thesis submitted by Thomas J. Sworski in partial fulfillment of requirements for the degree of Doctor of Philosophy at the University of Notre Dame.

(3) Sinclair Fellow.

(4) R. R. Hentz and M. Burton, THIS JOURNAL, **73**, 532 (1951).