mercial grade of pepsin was several times higher than that of the original pepsin, indicating a selective adsorption of the active pepsin into the monolayer on water or into that adsorbed on the conditioned plate.

SCHENECTADY, N. Y. RECEIVED MARCH 15, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Some Reactions of Indene Chloride and the *cis*- and *trans*-Chlorohydrins. Mechanism of Ketone Formation

BY C. M. SUTER AND GARSON A. LUTZ

It was reported by Spilker[1] many years ago that indene in dry ether adds chlorine to give an unstable oil which hydrolyzes readily to a chlorohydrin when boiled with 20% alcohol. Although the chlorination of indene, or of a coal tar fraction containing indene, has been mentioned by other investigators[2] in no case has the indene chloride been described. Courtot and co-workers[2c] were able to isolate a second chlorohydrin from the hydrolysis products and show that it was a stereoisomer of the one obtained by Spilker[1] since both compounds gave 2-chloro-1-indanone when oxidized with chromic acid.

Indene Chloride.[3]—The addition of chlorine to indene in carbon tetrachloride at a low temperature gives an 80% yield of the chloride together with a small amount of 2-chloroindene and higher chlorination products. A careful refractionation of a sample of the chloride indicated that it was homogeneous rather than a mixture of stereoisomers. The formation of two chlorohydrins on hydrolysis does not contradict this since it has been noted[4] that the solvolysis of active α-chloroethylbenzene is accompanied by partial racemization and the α-chlorine of indene chloride would be expected to act similarly. Attempts to obtain a second indene chloride apparently were not successful. The compounds obtained by the action of phosphorus pentachloride upon the higher melting (*trans*) chlorohydrin and of thionyl chloride upon both *cis*- and *trans*-chlorohydrins showed small variations in refractive index but had identical boiling points and upon hydrolysis all gave a mixture of chlorohydrins in which the *trans* isomer predominated. In a recent[5] discussion of reactions where hydroxyl is replaced by chlorine it was noted that thionyl chloride always reacts without inversion when the hydroxyl is attached to a carbon adjacent to phenyl if the reaction is carried out in the absence of a base. If this rule holds for the indene chlorohydrins the isomeric chlorides are indistinguishable in their common physical properties and in their behavior on hydrolysis, an unlikely circumstance. Bodendorf and Böhme[6] have found that an active form of α-chloroethylbenzene is racemized by a variety of chlorides in polar solvents. A preliminary experiment with indene chloride and mercuric chloride in nitromethane gave a product with a refractive index slightly lower than that of the original but the change was too small to be regarded as significant. Apparently the only *cis*- and *trans*-halides of a cyclic olefin that have been isolated are those obtained from cyclohexene and chlorine in the presence of cuprous chloride.[7] Cyclohexene bromide has given every indication of being homogeneous[8] and is probably the *cis* isomer. Cyclopentene likewise gives only one bromide.[9]

Indene chloride decomposes when heated to 225-235° with vigorous evolution of hydrogen chloride and formation of 2-chloroindene. A trace of the olefin is produced when the chloride is distilled at much lower temperatures as shown by refractionation of the distillate. The position of the chlorine is evident since the same compound results from dehydration of the indene chlorohydrins. Von Braun and Ostermayer[10] recently have reported the preparation of 3-chloroindene but

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(1) Spilker, *Ber.*, **26**, 1538 (1893).

(2) (a) Heusler and Schieffer, *ibid.*, **32**, 30 (1899); (b) Weissgerber, *ibid.*, **44**, 1442 (1911); (c) Courtot, Fayet and Parant, *Compt. rend.*, **186**, 371 (1928).

(3) Since the halides obtained from olefins necessarily contain two halogen atoms the prefix di- is omitted here as it is in ethylene chloride. Confusion with the possible but unknown higher chlorides of indene seems unlikely.

(4) Steigman and Hammett, THIS JOURNAL, **59**, 2536 (1937).

(5) Cowdrey, Hughes, Ingold, Masterman and Scott, *J. Chem. Soc.*, 1266 (1937).

(6) Bodendorf and Böhme, *Ann.*, **516**, 1 (1935).

(7) Komatsu and Kawamato, *J. Chem. Soc. Japan*, **52**, 685 (1931); *C. A.*, **26**, 5080 (1932).

(8) Rothstein, *Ann. chim.*, **14**, 542 (1930).

(9) Zelinski and Levina, *Ber.*, **66B**, 477 (1933).

(10) Von Braun and Ostermayer, *ibid.*, **70B**, 1006 (1937).

the 1-chloroindene is unknown. Reaction of 2-chloroindene with one mole of hydrogen in the presence of a platinum catalyst gave equimolecular amounts of indane and unchanged olefin. The 2-chloroindene is slowly resinified by concentrated sulfuric acid but the change occurs much more slowly than it does for indene.

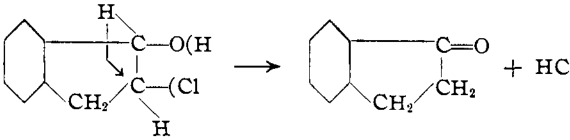
The maximum amount of low-melting (*cis*) chlorohydrin isolated using the method of Courtot[2c] corresponded to a 10% yield. No 2-chloroindene was found among the by-products of the hydrolysis reaction. Ward[11] observed that α-chloroethylbenzene upon hydrolysis gives considerable styrene but the behavior of 1-chloroindane is not known hence no conclusions can be drawn regarding the relative effects of the second halogen atom and the ring structure in inhibiting olefin formation. Since the *cis*-chlorohydrin decomposes spontaneously into 1-indanone, this latter is a minor product of the hydrolysis.

Indene Chlorohydrins.—It was suggested some time ago[12] that the higher melting indene chlorohydrin is the *trans* isomer. To obtain evidence on this point the properties of the two compounds have been investigated in detail.

The *cis*- and *trans*-cyclopentene[13] and methylcyclopentene[14] chlorohydrins differ considerably in boiling point, possibly due to hydrogen bond formation[14] in the case of the *cis* isomers. In accord with these observations at 20 mm. the *trans*-indene chlorohydrin boils some 7° higher than the *cis* compound. It is to be noted that the chlorohydrins do not follow the boiling point rule common to certain other classes[15] of *cis-trans* isomers. Bartlett[16] found the *cis*- and *trans*-cyclohexene chlorohydrins to have the same boiling point although Godchot, Mousseron and Granger[13] report a 10° difference at 15 mm. for two compounds obtained from cyclohexene and hypochlorous acid.

Spontaneous decomposition of the *cis*-chlorohydrin into 1-indanone occurs at an appreciable rate in water solution at 80° or above. While the reaction is accelerated greatly by alkali the rate is not affected by the presence of acid except indirectly by removing the chlorohydrin through side reactions. In a solution maintained just alkaline to phenolphthalein at 100° the transformation was 50% complete in twenty minutes while in a mixture slightly alkaline to methyl red–methylene blue only 5% of the chlorohydrin reacted in this time. Small yields of 1-indanone dinitrophenylhydrazone were isolated after heating the chlorohydrin with 2.9 and 4.5 N sulfuric acid at 100° for three hours. Rate determinations made at 79.6 ± 0.2° showed that the reaction was of the first order and proceeded at the same initial rate in water, 0.01 N hydrochloric acid, or 0.059 N potassium nitrate. The drift in the apparent value of k_1 for the more dilute chlorohydrin solutions (0.2 g./100 cc. solution) was slight but in higher concentrations and particularly with acid present at the start the change was appreciable, the value of k_1 dropping from 1.40 to 1.21×10^{-4} by the time the reaction was about 50% complete. It is not known at present what causes the apparent change in k_1 but it may be conversion of the chlorohydrin into the ether since Ward[11] has observed that phenylmethylcarbinol is largely converted into its ether by refluxing with 0.5 N hydrochloric acid. Conversion of the indene chlorohydrin to 1-indanone proceeds about one fourth as rapidly in 47.5% aqueous alcohol as in water.

The effect of solvent and the lack of effect by acid are characteristics associated with a solvolysis reaction[17,18] for which it has been suggested[4] that the "driving force" is the energy of solvation of the halide ion. The formation of the ketone may be looked upon as resulting from three simultaneous changes: the loss of hydrogen and chloride ions and the transfer of a hydrogen with its electron pair, the transfer resulting in inversion of carbon 2. From this mechanism it is clear that the reaction will be facilitated by hydroxyl and other basic ions, possibly because of the formation of highly reactive alcoholate ions in which the negatively charged oxygen repels the migrating hydrogen and its electron pair. Similarly the reaction should be in-



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(11) Ward, *J. Chem. Soc.*, 445 (1927).

(12) Porter and Suter, THIS JOURNAL, **57**, 2024 (1935).

(13) Godchot, Mousseron and Granger, *Compt. rend.*, **200**, 748 (1935).

(14) Bartlett and White, THIS JOURNAL, **56**, 2785 (1934).

(15) Hückel, "Theoretische Grundlagen der organischen Chemie," 2d ed., Akademische Verlagsgesellschaft m. b. H., Leipzig, 1935, Vol. II, p. 125.

(16) Bartlett, THIS JOURNAL, **57**, 224 (1935).

(17) Hughes, *J. Chem. Soc.*, 255 (1935).

(18) Olson and Halford, THIS JOURNAL, **59**, 2644 (1937).

creased in rate by any positive ion or any molecule that will aid in removal of the halogen. Silver[19] ions show this property,[20] the reaction being rapid for halides that readily undergo solvolysis. As was anticipated dilute (0.059 *N*) silver nitrate caused a five-fold increase in the rate of formation of 1-indanone at 80°. It is probable that part of this effect was due to solid silver chloride catalysis but this was not investigated. As would be expected from the mechanism suggested the formation of 1-indanone does not occur readily for the *trans*-chlorohydrin. The effect of silver nitrate upon the *trans* compound is negligible under conditions resulting in a rapid conversion of the *cis*-chlorohydrin to ketone. Tiffeneau and co-workers have found[21] that *trans*-[22]iodohydrins of cyclopentene and indene are converted either to the oxides or to glycols or their mononitrates when acted upon by silver nitrate. The diversity of products obtained from a straight chain iodohydrin depends upon its ability to react in both *cis* and *trans* positions. Thus allylbenzene iodohydrin[23] by the *cis* reaction yields methyl benzyl ketone, by the *trans* reaction allylbenzene oxide and glycol. Since α-iodobenzyldimethylcarbinol[24] with silver nitrate yields methyl α-phenylethyl ketone with migration of a methyl group it would be anticipated that the *cis* chlorohydrins investigated by Bartlett[25,14,16] would be converted into ketones by this reagent.

In an aqueous solution maintained slightly alkaline to phenolphthalein at 100°, *trans* indene chlorohydrin rapidly loses hydrogen chloride with formation of a mixture in which 2-indanone is the chief component. The oxide is undoubtedly an intermediate since this is known[26] to yield the ketone under a variety of conditions. In water the chlorohydrin hydrolyzes until the solution becomes slightly acidic to methyl red whereupon the reaction becomes extremely slow. At 80° it did not proceed beyond 1% in eight hours. In 0.2 *M* sodium acetate 72% of the chlorohydrin was converted into a mixture of *cis*- and *trans*-glycols in fourteen hours at 100°. It has been reported[27] that in dilute hydrochloric acid solution hydrolysis to the *cis*-glycol occurs. In our experience a mixture of the two isomers always results. This is to be expected, regardless of which glycol is the primary product, since the two glycols have been shown[28] to be interconvertible by dilute acid.

In an earlier investigation[12] it was observed that *trans*-indene bromohydrin is converted into 1-indanone by dilute sulfuric acid. The chlorohydrin undergoes this reaction slowly, a 7% yield of 1-indanone dinitrophenylhydrazone being isolated after heating 0.1 g. with 50 cc. of 4.5 *N* sulfuric acid for three hours. (Under the same conditions the *cis*-chlorohydrin gave a 14.5% yield of the 1-indanone.) It has been suggested[12] that this reaction occurs through an intermediate having a carbon atom with an "open sextet." An interesting alternative mechanism calls for the *trans* migration of a hydrogen with its electron pair, the halogen being lost through an inversion reaction. A choice between these two processes is not possible at present and there is no obvious reason why either should be facilitated by hydrogen ions. This type of ketone formation from a halohydrin will be investigated further.

Experimental

Indene Chloride.—Dry chlorine was passed into a well-cooled solution containing 1560 g. (13.45 moles) of indene in 4 kg. of carbon tetrachloride until the increase in weight corresponded to the theoretical amount (950 g.). The solvent was distilled off and the remaining yellow liquid fractionated under diminished pressure through a one-meter column fitted with a partial condensation head. The fore-run (50 cc.) consisted of indene and 2-chloroindene. The portion distilling at 98–102° (5 mm.) analyzed correctly for indene chloride. The yield was 2030 g. or 80% of the theoretical amount of material with $n^{25}\text{D}$ 1.5710 and $d^{25}{}_4$ 1.249.

Anal. Calcd. for $C_9H_8Cl_2$: Cl, 37.9. Found: Cl, 38.1. A careful refractionation of a sample of this material gave a pure product distilling at 83–85° (3 mm.), $n^{25}\text{D}$ 1.5690, $d^{25}{}_4$ 1.254, free from 2-chloroindene and higher chlorination products. Except for the first, successive fractions showed no variation in refractive index, hence it is believed that only one isomer was present.

Pyrolysis of Indene Chloride.—Heating 150 g. (0.8 mole) of the chloride in a 200-cc. flask for five hours at 225–235° resulted in vigorous evolution of hydrogen chloride. Fractionation of the residue gave 45 g. (37%) of 2-

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(19) The effect of other positive ions and of molecules on this reaction will be reported elsewhere.

(20) The earlier reports on this effect were by Burke and Donnan, *J. Chem. Soc.*, **85**, 555 (1904); *Z. physik. Chem.*, **69**, 148 (1909); Donnan and Potts, *J. Chem. Soc.*, **97**, 1882 (1910).

(21) Tiffeneau, *Compt. rend.*, **159**, 771 (1914); *Bull. soc. chim.*, **15** 79 (1914); Tiffeneau and Orékhoff, *ibid.*, **27**, 783 (1920).

(22) This configuration is assumed because of the preparation method employed.

(23) Porcher, *Bull. soc. chim.*, **31**, 334 (1922).

(24) Tiffeneau and Orékhoff, *Compt. rend.*, **172**, 387 (1921).

(25) Bartlett and Rosenwald, THIS JOURNAL, **56**, 1990 (1934).

(26) Böeseken and Van Loon, *Proc. Acad. Sci. Amsterdam*, **20**, 1186 (1.19); *C. A.*, **13**, 814 (1919).

(27) Korpukhin, Duimarskaya and Halbershtadt, *C. A.*, **29**, 623 (1935).

(28) Hermanns, *Z. physik. Chem.*, **113**, 365 (1924); *Ber.*, **57**, 824 (1924).

chloroindene, b. p. 95–98° (11 mm.), n^{25}_D 1.5824. This solidified in the refrigerator and when recrystallized from methanol by cooling in dry ice and acetone melted at 17–18°.

Anal. Calcd. for C_9H_7Cl: Cl, 23.6. Found: Cl, 23.5.

Hydrolysis of Indene Chloride.—Refluxing 125 g. (100 cc.) of indene chloride with 500 cc. of water and 250 cc. of 95% alcohol for seven and one-half hours gave upon cooling 86 g. of crude chlorohydrins. The filtrate gave a precipitate of 1-indanone dinitrophenylhydrazone when tested with 2,4-dinitrophenylhydrazine reagent. Recrystallizing the chlorohydrins from 225 cc. of benzene gave 40 g. of the *trans* isomer, m. p. 123–124°, after the second crystallization. A small sample of this was found to distil at 157° (20 mm.). The residue from the first filtrate was crystallized twice from dry ether (100 cc.) at about 0°, giving 6.5 g. of *cis*-chlorohydrin, m. p. 110–111°. In a run using 215 cc. of indene chloride the yield was 14 g., m. p. 110–111°, and 9 g. of a second crop, m. p. 105–108°, or a total of 9.5% of the theoretical amount. A small sample of the pure compound distilled at 150° (20 mm.).

Fractionation of the oily by-products of the hydrolysis gave 5 g., b. p. 105–142° (15 mm.), which was chiefly 1-indanone, b. p. 117–118° (15 mm.), and a mixture of higher boiling products which was not further investigated. No 2-chloroindene was noted.

Dehydration of the Chlorohydrins.—Treating 11 g. of the *trans*-chlorohydrin dissolved in 75 cc. of carbon tetrachloride with 8 g. of phosphorus pentoxide and warming for fifteen minutes gave 3.9 g. (41%) of 2-chloroindene, b. p. 58–62° (3 mm.), m. p. 17–18°. A mixed m. p. with that obtained from pyrolysis of indene dichloride showed no depression. Dehydration of the *cis*-chlorohydrin by the procedure just described gave also 2-chloroindene.

In another experiment refluxing 5.6 g. of *trans*-chlorohydrin in 150 cc. of carbon tetrachloride with 14 g. of phosphorus pentoxide for one hour gave a viscous oil, b. p. 153–155° (3 mm.), which solidified upon cooling in the refrigerator.

Anal. Calcd. for $C_{18}H_{16}OCl_2$: Cl, 22.24. Found: Cl, 22.46.

The ether reacted with bromine with evolution of hydrogen halide. Upon distilling at atmospheric pressure it decomposed to give 2-chloroindene, m. p. 17–18°.

Reduction of 2-Chloroindene.—To 45 cc. of absolute alcohol containing 90 mg. of Adams platinum catalyst was added 14.5 g. of 2-chloroindene. Reduction was effected under about 30 lb. (2 atm.) pressure until the theoretical amount of hydrogen had been absorbed to convert the 2-chloroindene to 2-chloroindane. (The apparatus was standardized against pure indene.) After filtering, the solvent was distilled off and the residue fractionated. Equivalent amounts of indane, b. p. 69–72° (20 mm.), and 2-chloroindene, b. p. 93–95° (12 mm.), were obtained. A strong odor of hydrogen chloride was observed when the reduction bottle was opened. The indane contained no trace of indene as it was not changed by cold concentrated sulfuric acid.

Conversion of the *cis*-Chlorohydrin to 1-Indanone. A. Reaction with Dilute Alkali.—To 100 cc. of water at the boiling point (99.3°) was added 0.422 g. of chlorohydrin and three drops of phenolphthalein indicator. One-tenth normal sodium hydroxide solution was then added dropwise at such a rate as to maintain a slight pink color in the reaction mixture. The reaction was 52% complete in twenty minutes and 99.1% complete in eighty-five minutes. The control of the alkalinity was not sufficiently exact to warrant the calculation of a reaction rate constant. A 25-cc. portion of the reaction mixture was acidified with 3 cc. of concentrated sulfuric acid and 25 cc. of a dinitrophenylhydrazine solution[29] was added. After heating on the steam-bath, cooling and filtering through a sintered glass crucible, and drying at 125° in the oven there was obtained 0.169 g. of the crude hydrazone. This corresponds to 0.357 g. of ketone in the whole reaction mixture whereas the theoretical yield would call for 0.327 g. Separate experiments showed that the hydrazone is usually contaminated with a small amount of the dinitrophenylhydrazine when the latter is present in considerable excess.

B. Reaction in Slightly Acidic Solution.—In an experiment similar to A except for the use of methyl red-methylene blue[30] as indicator the reaction was 4% complete in twenty minutes, 9.2% in fifty minutes and 19.7% in one hundred and ten minutes, corresponding to a first order reaction with $k = 0.0020 \pm 5\%$.

C. Reaction in Strongly Acidic Solutions.—Heating 0.1087 g. of the chlorohydrin in 35 cc. of 2.92 *N* sulfuric acid for three hours and pouring the reaction mixture into 25 cc. of dinitrophenylhydrazine reagent gave 0.0144 g. of the hydrazone corresponding to a 7.2% conversion. In another run the yield was 8.8%, the product melting at 245–248° corr. and the mixed m. p. with an authentic sample[31] being 250–252°. Recrystallization from dioxane gave the pure hydrazone.

Heating 0.1058 g. of the chlorohydrin with 50 cc. of 4.51 *N* sulfuric acid for three hours at 100° gave a 14.5% yield of the dinitrophenylhydrazone. The solubility of the chlorohydrin in acid of this concentration is noticeably less than in water.

The question arose as to the effect of the 4.51 *N* sulfuric acid upon 1-indanone. Heating 0.1023 g. of the ketone with the acid at 100° for three hours and filtering the slightly murky reaction mixture into 25 cc. of ketone reagent gave 0.2080 g. of the hydrazone, an 86% recovery; when the heating was omitted the recovery was 94% or higher.

D. Reaction in Salt Solutions.—Experiments in which a 0.1 g. sample of the chlorohydrin was heated in 35 cc. of 0.0168 *N* potassium nitrate, silver nitrate, or silver sulfate solution showed that the rate of formation of 1-indanone was much accelerated by the silver salts and unaffected by the potassium nitrate as compared with the rate in water. In each instance the dinitrophenylhydrazone of the ketone was isolated and identified.

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(29) This was made by dissolving 5 g. of 2,4-dinitrophenylhydrazine in 35 cc. of concentrated sulfuric acid, adding the solution to 300 cc. of 95% alcohol and diluting to 500 cc. with water. Upon long standing some of the reagent may precipitate from the solution. Dilution of the solution with an equal volume of water gives a precipitate after standing for an hour but dilution with 3 *N* sulfuric acid does not.

(30) The methyl red decomposes slowly at 100° making it necessary to add more indicator occasionally.

(31) Allen, THIS JOURNAL, **52**, 2955 (1930). The pure compound melts at 258°.

E. Reactions at 79.6 ± 0.2°.—Rate determinations were made in an apparatus maintained at constant temperature by the vapor of boiling benzene. At suitable intervals samples were withdrawn, cooled and titrated with standard alkali. The solutions varied in initial concentration from about 0.2 to 0.4 g. of chlorohydrin/100 cc. Typical data are given in Table I. From these and other data it was found that the initial value of k_1 was $1.40 \pm 0.05 \times 10^{-4}$. The results of a run in which 0.0095 N hydrochloric acid was the solvent are listed in Table II.

TABLE I

Chlorohydrin, g./100 cc. soln.	Time, min.	Decomposition, %	$k_1 \times 10^4$
0.3892	2475	27.5	1.30
	5340	47.6	1.21
	5775	49.7	1.19
0.2102	1410	17.2	1.34
	3015	32.3	1.30
	4560	44.75	1.30

TABLE II

Chlorohydrin, g./100 cc. soln.	Time, min.	Decomposition, %	$k_1 \times 10^4$
0.3965	1045	13.3	1.37
	2310	25.3	1.26
	3825	36.2	1.18

For a run made in 0.2 N potassium chloride $k_1 = 1.50 \pm 0.03 \times 10^{-4}$, slightly higher than in water. In 0.059 N potassium nitrate the reaction was 5.7% complete in four hundred forty minutes, whereas in 0.059 N silver nitrate it was 30% complete. In a solution made from equal volumes of 95% ethyl alcohol and water k_1 was 0.34×10^{-4}.

Reactions of *trans*-Indene Chlorohydrin. A. Reaction with Alkali.—Titration of a 0.421-g. sample of the chlorohydrin in 100 cc. of water at 99.3° with 0.1 N alkali using phenolphthalein as indicator was complete in about ten minutes. The cloudy reaction mixture was cooled to room temperature and 50 cc. was extracted with ether. This gave a few crystals of crude 2-indanone, m. p. 45–55°. A 25-cc. portion of the reaction mixture was acidified with 3 cc. of concentrated sulfuric acid and added to 25 cc. of the dinitrophenylhydrazine reagent. There was obtained 0.109 g. of crude hydrazone corresponding to a 70% yield. This was undoubtedly higher than the actual yield because it included some amorphous colloidal material present in the reaction mixture as a by-product.

B. Reaction with Sodium Acetate.—To a solution of 2.72 g. (0.02 mole) of sodium acetate in 100 cc. of water was added 1.68 g. (0.01 mole) of the *trans*-chlorohydrin and the mixture refluxed for a total of fourteen hours. Titration showed the hydrolysis to be 72% complete. Filtering the cold solution gave 12% of unchanged chlorohydrin and evaporation of the filtrate to 15 cc. gave a fraction of nearly pure *trans*-glycol, m. p. 143–146°, and a second fraction of a mixture of glycols, m. p. 92–95°. No trace of a ketone was formed.

C. Reaction with Acid.—Heating 0.1166 g. of the chlorohydrin with 35 cc. of 2.92 N sulfuric acid at 100° for three hours gave 0.0151 g. of 1-indanone dinitrophenylhydrazone, m. p. 245–250°, corresponding to a 6.9% yield of ketone. A similar experiment employing 50 cc. of 4.5 N acid gave a 7.3% yield of the dinitrophenylhydrazone.

The *trans*-chlorohydrin did not hydrolyze perceptibly in eight hours at 80° in water. Heating a 0.1-g. sample with 35 cc. of 0.0168 N silver nitrate gave a negligible amount of silver chloride in three hours at 100°.

Indene Chloride from the Chlorohydrins. A. Reaction of the *trans*-Chlorohydrin with Phosphorus Pentachloride.—To a solution of 17 g. (0.1 mole) of the *trans*-chlorohydrin in 180 cc. of dry ether was added 21 g. (0.1 mole) of phosphorus pentachloride. After standing overnight the reaction mixture was washed with water, dried and distilled. The indene chloride distilled at 116–120° (13 mm.). The yield was 9.5 g. of product with $n^{25}\text{D}$ 1.5716. Hydrolysis of a 1-g. sample by refluxing with 100 cc. of water gave 0.48 g. of chlorohydrin, m. p. 115–120°. Ether extraction of the water gave 0.4 g. of pasty solid which when dried on filter paper melted at 90°. Hydrolysis of indene chloride from indene and chlorine gave identical results.

B. Reaction of Chlorohydrins with Thionyl Chloride.—Reaction occurred at once upon adding 9 g. of the *cis*-chlorohydrin to 10 cc. of thionyl chloride. After refluxing for a few minutes to complete the reaction the product was distilled. There resulted 7 g. of chloride, b. p. 122–123° (15 mm.) with $n^{24}\text{D}$ 1.5700. Hydrolysis of a 1-g. sample of this by boiling with 100 cc. of water for two and one-half hours and cooling the solution to room temperature gave 0.55 g. of chlorohydrin, m. p. 115–120°.

When the *trans*-chlorohydrin was the starting material the indene chloride distilled at 120–121° (14 mm.) and gave $n^{24.5}\text{D}$ 1.5700. Hydrolysis of a 1-g. sample gave 0.56 g. of chlorohydrin of m. p. 115–120° with slight softening above 105°. These results are nearly identical with those obtained from the hydrolysis of a sample of indene chloride obtained from indene and chlorine. Extraction of the hydrolysis filtrate with ether gave a pasty residue containing in addition to a mixture of chlorohydrins a small amount of 1-indanone.

Summary

1. The report that hydrolysis of indene chloride yields two chlorohydrins has been verified. Dehydration of these and also the pyrolysis of indene chloride yields 2-chloroindene.

2. Reduction of 2-chloroindene with hydrogen and a platinum catalyst gives indane. 2-Chloroindene is much less readily polymerized by sulfuric acid than is indene.

3. *cis*-Indene chlorohydrin decomposes spontaneously in water solution at 80° or higher to give 1-indanone. The reaction is accelerated by alkali or silver salts, is unaffected by dilute acid and is slowed by using aqueous alcohol as the solvent.

4. *trans*-Indene chlorohydrin in dilute alkali gives a mixture of products of which one is 2-indanone, while it is slowly converted to 1-indanone by 2.9 or 4.5 N sulfuric acid at 100°. Aqueous sodium acetate gives a mixture of glycols.

5. Various samples of indene chloride obtained from (a) indene and chlorine, (b) *trans*-

indene chlorohydrin and phosphorus pentachloride and (c,d) both chlorohydrins and thionyl chloride show practically identical physical properties and upon hydrolysis all give the *trans*-chlorohydrin as the chief product.

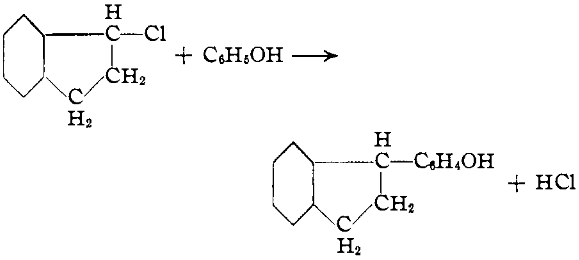
EVANSTON, ILLINOIS RECEIVED APRIL 7, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Reaction of Indene Chloride with Phenols

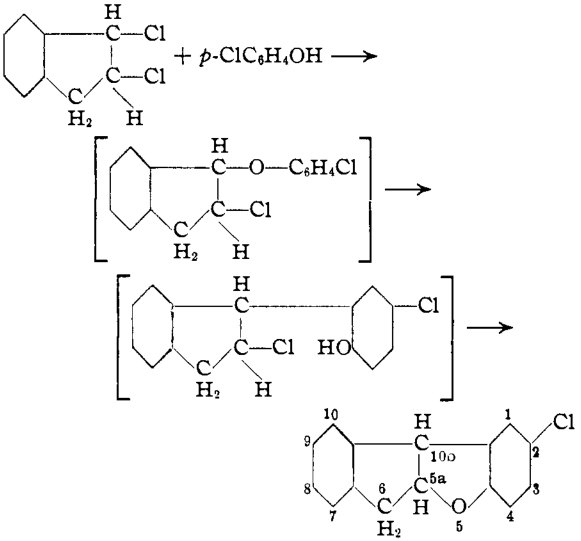
BY C. M. SUTER AND GARSON A. LUTZ

It was observed by Claisen[1] that benzyl chloride reacts readily with the sodium salt of a phenol in a non-polar solvent to give the *o*-benzylphenol rather than the ether. More recently[2] it has been shown that benzyl chloride reacts with excess phenol at temperatures above 125° to yield a mixture of *o*- and *p*-benzylphenol together with some dibenzylated product. This procedure had been mentioned previously by Courtot[3] and also in the patent literature[4] but without experimental details. Courtot[3] likewise reported that 1-chloroindane reacts with phenol in ether or benzene solution even at 15°, para substitution occurring. There are several patents describing the condensation of indene with phenols by means of acids;[5] presumably here also an intermediate indane derivative is involved.



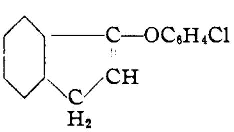
In the present investigation it has been found that indene chloride reacts readily with phenol, *m*- and *p*-cresol, and *p*-chlorophenol when the halide is added to an excess of the phenol at 145° or above with evolution of *two molecules* of hydrogen chloride. Fractional distillation of the resulting mixture after removal of the excess phenol gives in each case at least three compounds: a saturated ether containing one indane and one phenolic residue, an unsaturated phenol, and a high-boiling substance containing two phenolic groups. In the case of phenol this last material greatly predominates while for the cresols and *p*-chlorophenol the ether is obtained in considerable amount.

Taking into account the reactivity of the chlorine atom adjacent to the aromatic ring in the indene chloride the reaction with *p*-chlorophenol may be assumed to proceed as shown in the equations.

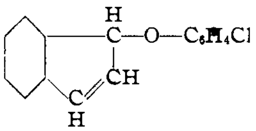


I

The evidence available concerning the nature of the ether (I) is in accord with the proposed structure. That the ether linkage is more stable than would be expected for an indenyl *p*-chlorophenyl ether (II or III) is shown by its inertness toward hydrogen iodide at high temperatures. The reaction with bromine occurs with evolution of



II



III

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(1) Claisen, *Ann.*, **442**, 237 (1925).

(2) McMaster and Bruner, *Ind. Eng. Chem.*, **28**, 505 (1936).

(3) Courtot, *Compt. rend.*, **187**, 661 (1928).

(4) Kalle and Company, German Patent 346,384; *Frdl.*, **14**, 1200 (1926).

(5) I. G. Farbenind, A.-G., French Patent 636,606, *C. A.*, **23**, 607 (1929); French Patent 39,642, *ibid.*, **26**, 4827 (1932); British Patent 297,075, *ibid.*, **23**, 2539 (1929); Müller and Kirchner, German Patent 499,587, *ibid.*, **24**, 4524 (1930); Rosenthal and Kropp, U. S. Patent 1,754,052, *ibid.*, **24**, 2549 (1930).