

Summary

1. Certain keto-chlorimines have been prepared by the action of chlorine on nitrogen-magnesium compounds of the type $R'R''C=NMgX$, which may readily be obtained from Grignard reagents and nitriles.

2. The action of chlorine on the nitrogen-magnesium compound obtained from phenylmagnesium bromide and *p*-chlorobenzonitrile yields *p*-chlorobenzophenone chlorimine, m. p. 104°. No stereoisomer has been isolated.

3. The action of chlorine on the nitrogen-magnesium compound obtained from *p*-chlorophenylmagnesium bromide and *p*-chlorobenzonitrile yields *p,p'*-dichlorobenzophenone chlorimine, m. p. 74°.

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[CONTRIBUTION FROM THOMAS AND HOCHWALT LABORATORIES, INC.]

POLYMERIZATION OF DIOLEFINS WITH OLEFINS. I. ISOPRENE AND PENTENE-2

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When anhydrous aluminum chloride is placed with pure isoprene in which there is no appreciable amount of olefin present, and the mixture shaken, there is no temperature rise or any other obvious chemical reaction even when a considerable portion of anhydrous aluminum chloride has been added. Upon prolonged standing slow polymerization takes place, producing mainly the insoluble polymer described below. If to this mixture a small amount of olefin, such as pentene-2 or trimethylethylene, is added and the mixture shaken, an obvious reaction starts immediately which becomes violent if much of the olefin has been added, and unless the mixture is cooled the products will soon boil away. This interesting reaction, some phases of which were also observed and discussed by Aschan,¹ has led to the following investigation.

If an equimolar mixture of isoprene and pentene-2 or trimethylethylene is diluted with an inert hydrocarbon solvent and the mixture cooled with constant stirring, there can be added portion-wise small amounts of anhydrous aluminum chloride. After several hours a point is reached where there is no more evolution of heat. From the reaction mixture there is obtained, after decomposition of the aluminum chloride complex, two organic polymers, one soluble, the other insoluble in hydrocarbon solvents.

Soluble Polymer.—This polymer ranges from a viscous oil to a hard resin, depending upon the proportions of the olefin and diolefin employed and the subsequent treatment to which the product is subjected. The

¹ Aschan, *Chem. Abstracts*, **14**, 3823 (1916); *Ofversigi Finska Vetenskaps Soc.*, **58**, 42 (1916).

product consists of a mixture of higher oils and a hydrocarbon resin, the hardness depending upon the amount of oils removed. The color of the resin ranges from light straw to dark brown, the darker color resulting from elevated or prolonged heating in removing the associated oils. If low boiling inert solvents are used, such as hexane, a harder resin can be obtained with less heating as the solvent can be taken off at a lower temperature and its high vapor pressure helps to distil the associated oils. The resin is soluble in most hydrocarbon solvents such as gasoline, benzene, toluene, chlorinated hydrocarbon solvents, and drying oils such as linseed and china wood oil. It is virtually insoluble in ethyl and methyl alcohol and acetone and can be precipitated out of the hydrocarbon solution by them. It is also difficultly soluble in ethyl acetate but appreciably soluble in the higher acetates such as butyl and amyl. It has been found that when this resin polymer is exposed in a thin film to air it slowly oxidizes, becoming harder upon oxidation. A thin film was obtained by flowing on a glass plate a solution of the resin polymer in benzene and allowing the solvent to evaporate, and the iodine and acid numbers of portions of the film were taken and recorded daily. Initially the iodine value was 202 and the acid value 0.4, but after twenty-seven days the iodine value had irregularly fallen to 136 and the acid number risen to 16. After this apparently an equilibrium was reached and the polymer did not change appreciably. Ozone is absorbed rapidly at first when bubbled through a solution of this polymer in carbon tetrachloride, the absorption slowing down and finally stopping, yet the iodine number of the solution in some cases was as high as 140. If the carbon tetrachloride is distilled off there remains a brittle amorphous yellow solid which is now insoluble in carbon tetrachloride. This indicates that further polymerization has taken place during the heating to remove the solvent.

Insoluble Polymer.—This polymer occurring with the residue filtered from a solution of the above-described soluble polymer is freed from inorganic matter by repeatedly digesting and washing with 10% hydrochloric acid and water. There remains on drying at low temperatures, a white, granular organic polymer which by combustion was proved to conform to the formula $(C_5H_8)_x$. No molecular weight has yet been determined, as this polymer is characterized by its extreme insolubility, having been found insoluble in the solvents tried, with the exception of nitrobenzene and some of the higher amines in which it is only very slightly soluble. Strong acids decompose the product and phenols react giving a reddish-violet coloration with decomposition. This polymer begins to depolymerize when heated to around 116° . It first contracts, becoming more spongy and rubbery, and changes to a tan or brown color with small globules of oil being formed. On continuing the heating to 299° the whole mass begins to fuse and slowly changes to a dark heavy oil with some foaming which on cooling

solidifies to a transparent dark resin which is soluble in most hydrocarbon and chlorinated hydrocarbon solvents.

By varying the amounts of olefin polymerized with the isoprene, under the conditions recorded below, various amounts of the two polymers can be obtained as shown in Fig. 1, in which pure pentene-2 was polymerized in varying molar amounts with a mole of isoprene. The ordinates of the

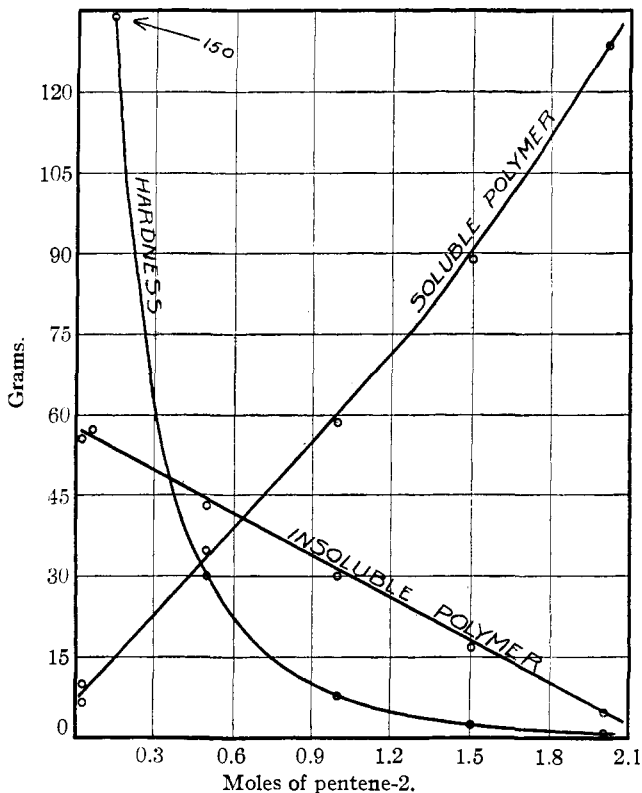


Fig. 1.—Yield of soluble and insoluble polymers formed when pentene-2 is varied, keeping isoprene constant at 1 mole. Variation in hardness of soluble polymer.

curve marked "Soluble Polymer" show the increase in grams of this polymer proportional to the pentene-2 used up to two moles, while the curve "Insoluble Polymer" shows the reverse relationship. When pentene-2 alone is polymerized with anhydrous aluminum chloride, no insoluble polymer is obtained, the product being an oil consisting of the various polymers of the olefin.² It appears therefore that the "Insoluble Polymer" curve approaches zero as a limit. The hardness of the soluble polymer is shown by

² F. W. Sullivan, Jr., V. Voorhees, A. W. Neeley and R. V. Shankland, *Ind. Eng. Chem.*, **23**, 604-611 (1931).

the lower curve, the ordinates of which are the reciprocals of the penetration value as measured by the A. S. T. M. penetration apparatus at 0° and 200 g. for sixty seconds, multiplied by 150. As can be seen, the hardness of the polymer rapidly decreases with the amount of pentene-2 in the mix. The product with two moles of the olefin is a heavy oil at the arbitrary end-point of hardening at 190°. By heating the product to a higher temperature or placing it under a vacuum, more of the oils can be distilled off, the polymer likewise being harder. However, if the temperature is taken too high, depolymerization starts as in the case of the insoluble polymer.

In this work no isoprene could be obtained which did not contain a small amount of olefin, so it is not known whether chemically pure isoprene polymerized under the prescribed conditions would give zero amount of soluble polymer. If this is the case, the whole "Soluble Polymer" curve would move down as the same isoprene was used for all points. The molecular weights on these soluble polymers vary from 845 to 1240 depending on the amount of lower polymers distilled from the resin. In general the more olefin present in the mixture, the lower the molecular weight. Likewise the combustions vary, the greater the amount of lower polymers removed, the closer the formula approaches to $(C_8H_8)_x$. Other diolefins and olefins give this characteristic reaction, the mechanism of which will be discussed in a later paper.

Experimental Procedure

The isoprene used was obtained by the destructive distillation of rubber, and the pentene-2 by dehydrating methylpropylcarbinol. The solvent was a paraffin hydrocarbon, boiling range 95–135°.

The mixture of isoprene, pentene-2 and solvent was carefully measured into a vessel equipped with a good agitator and cooled to 1°. At suitable intervals, depending on the temperature rise, approximately 0.8-g. portions of aluminum chloride were poured into the agitated mixture. When the reaction was nearly completed the catalyst was added in larger quantities, the temperature varying from 1 to 4°. The amount of aluminum chloride used was proportional to the isoprene and pentene-2 in the mix, 0.2 and 0.1 mole of aluminum chloride being used per mole of isoprene and pentene-2, respectively. The reaction mixture was agitated for twelve hours, after which an alcohol-aqueous ammonia mixture was used for neutralization and precipitation of the catalyst and insoluble polymer. The products were separated by filtration. The precipitate after digestion with 10% hydrochloric acid was washed well with water, dried and weighed. The filtrate was evaporated to recover the soluble polymer. When reduced to a small volume the solution was heated in an electric furnace at a uniform temperature of 190° for forty-five minutes.

Ossian Aschan, *Chem. Abstracts*, **14**, 3654 (1916); *Ofversigi Finska Vetenskaps Soc.*, **58**, 122 (1915). Ossian Aschan, *Ann.*, **324**, 1 (1902). Wallace H. Carothers, *Chem. Rev.*, **8**, 353 (1931) (includes bibliography of 254 references). Gustav Egloff, *et al.*, *J. Phys. Chem.*, **35**, 1825 (1931) (includes bibliography of 159 references). Engler and Routala, *Ber.*, **43**, 388-397 (1910); **42**, 4613-4620 (1909); **42**, 4620 (1909). Gangloff and Henderson, *THIS JOURNAL*, **39**, 1420 (1917).

Summary

1. Isoprene and pentene-2 react in the presence of anhydrous aluminum chloride to form two polymers, one insoluble, the other soluble in hydrocarbon solvents.

2. The amount of the soluble polymer formed is a function of the pentene-2 present. The hardness is an inverse function of the amount of pentene-2 present.

3. The amount of the insoluble polymer is an inverse function of the pentene-2 present.

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ALKAMINE ESTERS OF AROMATIC ACIDS: NOVOCAINE ANALOGS. II¹

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A search of the chemical literature relating to the novocaine type of anesthetic reveals very few compounds of the type $-\text{O}(\text{CH}_2)_n\text{N}^{\overline{x}}_{\overline{y}}$. A small number² have been made by comparison with the number of the type with identical substituents.

The difficulty of preparing secondary amines with dissimilar alkyl groups appears to have inhibited the investigative curiosity of workers in this field.

A study of the effects on the properties of the novocaine class of compounds of groups of this sort seemed worth while when the influence of such arrangements in the properties of the barbituric acid type of hypnotics, *e. g.*, Ipral, Amytal, Luminal, etc., is considered. In the absence of any considerable number of trustworthy generalizations that relate chemical

¹ Brill, *THIS JOURNAL*, **47**, 1134 (1925).

² (a) Volwiler and Adams, U. S. Patent 1,476,934 (Dec. 11, 1923), have made γ -butylallyl, γ -*n*-propylallyl, γ -isopropylallyl and γ -isoamylallylaminopropyl esters of benzoic acid; (b) v. Braun and Kirschbaum, *Ber.*, **52**, 2011 (1919), described a phenyl analog of novocaine, namely, the β -*p*-aminophenylmethylaminoethyl ester of *p*-aminobenzoic acid; (c) v. Braun and Braunsdorf, *ibid.*, **54**, 208 (1921), listed β -ethylallyl, β -ethylstyryl and β -ethylfuromethylaminoethyl esters of *p*-aminobenzoic acid; (d) Thorp has patented the hydrochloride of the benzoic ester of 1-methylethylamino-3-methylethylamino-2-hydroxypropane, U. S. Patent 1,193,649 (Aug., 1916). These compounds are reported to possess anesthetic properties.