

Cyanoethylation of aldehyde IV with sodium hydroxide in aqueous *t*-butyl alcohol gave a higher proportion of diene V and of alcohol IXB; alcohol IXA was not isolated.

We tentatively suggest that steric factors are the principal cause of the reported  $\gamma$ -cyanoethylation: position 20 of the thermodynamically favored *s-trans* aldehyde (cf. partial formula B) (as well as of the *s-cis* isomer) is sterically hindered and, therefore, the attack on its mesomeric anion should take place preferably in position 16. Furthermore, the geometry of the *s-trans* aldehyde and of the derived anion is particularly well suited for the aldol cyclization of the intermediate addition product, leading to a stable six-membered ring. A detailed discussion will follow in a subsequent paper of this series. We shall also illustrate the scope and the limitations of the above-described reaction sequence on the basis of cyanoethylations with various types of  $\alpha,\beta$ -unsaturated aldehydes.

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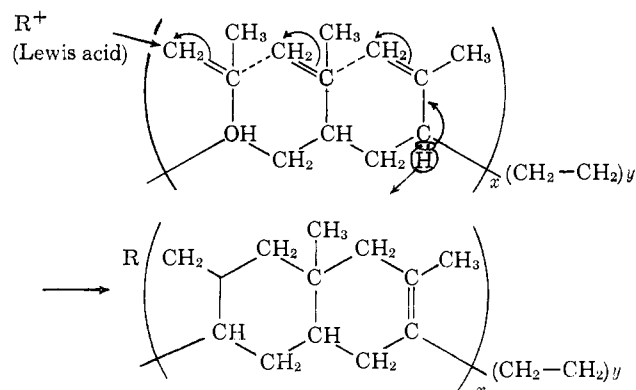
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#### THE PREPARATION AND CYCLIZATION OF A NOVEL COPOLYMER OF ETHYLENE AND ISOPRENE

Sir:

We wish to report the preparation of a novel copolymer of ethylene and isoprene, where the isoprene was copolymerized primarily through the 3,4 unsaturation.<sup>1</sup> The resultant copolymer contained blocks of isoprene units principally in the form of isopropenyl groups separated by methylene groups. Lewis acids such as boron trifluoride or phosphorus oxychloride eliminated isopropenyl unsaturation *via* what we believe to be a cyclization mechanism, to give a unique product containing *linearly*<sup>2</sup> fused cyclohexane units. For example, the cyclization of three lateral isopropenyl groups in an ethylene-isoprene copolymer probably takes place as shown.



The proposed structures of the products rely on the method of formation, X-ray and infrared analysis, and elemental analysis of nitrogen dioxide adducts.

The polymerizations were carried out by adding ethylene (100–300 cc./min.) and isoprene (0.5–2.0 cc./min.) to a stirred mixture of 1.5 l. of tetrachloroethylene,

(1) After this work was completed, G. Natta and L. Porri reported the preparation of 3,4-polyisoprene (French Patent 1,154,938) using tetraisopropyl titanate and aluminum triethyl as catalyst.

(2) The acid catalyzed cyclization of natural rubber (poly-1,3-isoprene) has been reported to give an *angular* polycycloisoprene with tricyclic and bicyclic segments, as evidenced by identification of aromatized fragments (F. T. Wallenberger, *Monatsh.*, **93**, 74, 1962). N.m.r. studies by M. A. Golub and J. Heller suggested that the structure is primarily bicyclic (*Chem. Eng. News*, October 15, 1962, p. 44).

5 of mmoles vanadyl trichloride, and 15 mmoles of aluminum triisobutyl, in the absence of oxygen and moisture. After 1.5 hours, the reaction was terminated by the addition of 50 ml. of methanol. The solid product was filtered off, washed successively with methanol and tetrachloroethylene, and then dried. This catalyst system polymerizes ethylene rapidly but is sluggish toward 1,4 addition polymerization of butadiene, which may help explain the preferential 3,4 polymerization of isoprene.

Over 95% of the isoprene units incorporated into the copolymer took the form of isopropenyl unsaturation (880 cm.<sup>-1</sup>) due to polymerization through the 3,4 unsaturation; only a trace of 1,4-isoprene unsaturation (835 cm.<sup>-1</sup>) was observed. Analysis of the isopropenyl unsaturation in the product showed that 10:1 mole ratio ethylene-isoprene mixtures produced copolymers which had a mole ratio of approximately 25:1. The unsaturation could not be removed by repeated precipitation from perchloroethylene, which suggests that the product was a copolymer and not an intimate mixture of homopolymers. X-Ray goniometer scans showed that the polyethylene crystallinity was virtually undisturbed, indicating the absence of random copolymer; this coupled with the ease of cyclization suggests that the isoprene was incorporated as a block.

Treatment of 1.5 l. of a 0.2% solution of the copolymer in perchloroethylene at 90° with 2 ml. of phosphorus oxychloride eliminated essentially all of the isopropenyl unsaturation in three minutes. Phosphorus could not be detected in the solid product, which was isolated by cooling, filtration, washing with methanol and drying. The formation of isopropylidene unsaturation instead of a polycyclic can be ruled out because (a) C=C stretching frequencies (1600–1650 cm.<sup>-1</sup> region) which were present in the untreated copolymer were absent after treatment with Lewis acid and (b) treatment of the product with the double bond reagents bromine or nitrogen dioxide gave adducts with a very low, non-stoichiometric bromine or nitrogen content. The isopropenyl groups of the uncyclized polymer are ideally situated for intramolecular cyclization of fused six-membered rings. This reaction is analogous to the rapid cationic polymerization of isobutylene.

Treatment of the cyclized 25:1 ethylene-isoprene copolymer with excess nitrogen dioxide gave an adduct which contained a maximum of 0.28% nitrogen. If the proposed cyclization mechanism is valid and nitrogen dioxide addition to the terminal unsaturated group in a block of fused rings was quantitative, this nitrogen content implies that there is one terminal unsaturated group remaining after cyclization of 13 isoprene units. In other words, the average block length in a 25:1 copolymer is 12 fused cyclohexane units.

Films of the cyclized ethylene-isoprene copolymer (2–6 mils, melt pressed at 175°) showed moduli (3% elongation) of 58 to 131 kp.s.i., an average elongation of about 100%, a tensile strength of 3 to 9 kp.s.i., and a pneumatic impact strength of 2–7 kg.-cm./mil. Polyethylene controls had moduli of about 100 kp.s.i., an elongation of 125%, pneumatic impact strengths of 1.5–2 kg.-cm./mil, and tensile strengths of 3 kp.s.i. or less.

Forthcoming reports from our laboratory will discuss the work in detail as well as the preparation and structure proof of cyclized poly(3,4-isoprene) polymers.

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