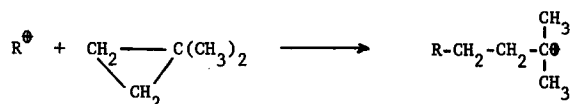


THE CATIONIC OLIGOMERIZATION OF ISOPROPYLCYCLOPROPANE

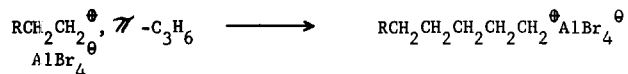
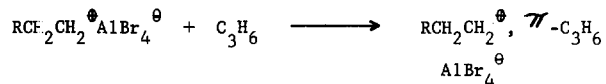
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Recent studies of the cationic polymerization of cyclopropane and alkyl substituted cyclopropanes have emphasized the carbonium ion nature of the intermediates involved in propagation. Ketley (1) has depicted the cleavage of the cyclopropyl ring in 1,1-dimethylcyclopropane as involving attack by a carbonium ion:



Tipper and Walker (2) have studied the kinetics of the polymerization of cyclopropane by $\text{AlBr}_3\text{-HBr}$ in heptane between 0° and -78°C . They postulated that the polymerization of cyclopropane proceeded by a carbonium ion mechanism in a manner similar to that of propylene and other Friedel-Crafts olefin polymerizations. The propagation was described as involving the formation of a growing chain-monomer π -complex, which then rearranged to a higher carbonium ion:



This mechanism is analogous to that suggested previously for the polymerization of propylene at low temperature with $\text{AlBr}_3\text{-HBr}$ (3).

Evidence is presented here which shows that the polymerization of isopropylcyclopropane with AlBr_3 does not involve carbonium ions of the type which occur during the cationic polymerization of olefins such as 3-methylbutene-1 and 4-methylpentene-1 under similar conditions.

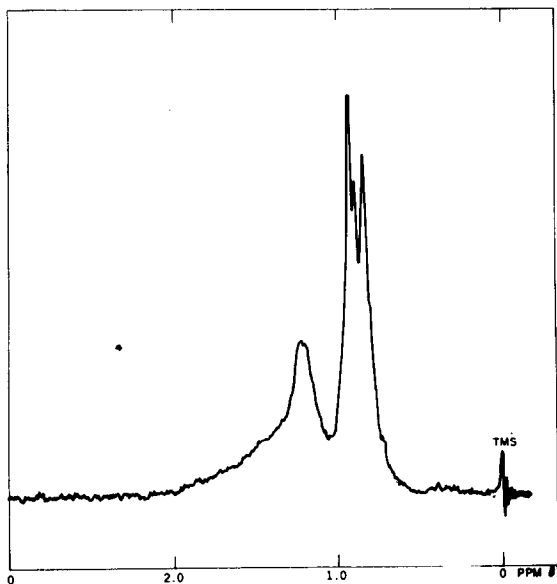
Isopropylcyclopropane^(a) was prepared by the method of Pines, Huntsman and Ipatieff (4). The monomer was polymerized with 2.8 mole % AlBr_3 at a temperature which varied from -50°C . to -10°C . The product was a clear, pale yellow liquid. Two samples of polymer prepared in different runs showed degrees of polymerization (D.P.) of 3.4 and 4.2 as measured by ebulliometry and V.P. osmometry. The low D.P. may be attributed to hydride transfer from monomer. This would account for the lack of unsaturation in the polymer as shown by NMR. Fontana and coworkers (3) noted that the molecular weight of polypropylene was lower when prepared in the presence of branched-chain hydrocarbons as contrasted with n-butane as solvent, and attributed this to hydride-ion transfer to the growing carbonium ions.

(a) The monomer had b.p. $57\text{-}59^\circ$, n_D^{20} 1.3868. The following properties have been reported: b.p. $58.3\text{-}58.5^\circ$ (750 mm.), n_D^{20} 1.3857 (4); b.p. $58,31^\circ$ (760 mm.), n_D^{20} 1.3865 (5). The infrared spectrum of the monomer showed a strong peak at 9.8μ . The absorption peak has been reported for isopropylcyclopropane and is characteristic of the cyclopropyl ring generally (6). Further analysis of the monomer by gas chromatography on a 2 m. Ucon (Perkin-Elmer R) column at 28°C . and a 15 ft. 20% AgNO_3 -propylene glycol on chromosorb P (acid washed) column at 28°C . revealed only trace amounts of impurities present.

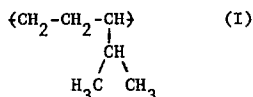
The infrared spectrum of the polymer was relatively simple and showed very strong absorption in the C-H stretching region 2830 cm^{-1} to 2930 cm^{-1} , strong absorption at 1458 cm^{-1} (CH deformation of methyl and methylene) and a doublet centered at 1371 cm^{-1} (due to $\text{C}(\text{CH}_3)_2$ of the isopropyl group). Weak bands attributed to the isopropyl group (7) were also present at 1165 cm^{-1} and 914 cm^{-1} .

NMR spectra of the polymers were obtained with 15% carbon tetrachloride solutions at frequencies of 60 Mc (Fig. 1) and 100 Mc. The only absorptions found were in the methyl, methylene and methine region.

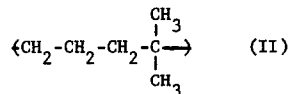
Figure 1
NMR SPECTRUM OF CATIONIC POLY-ISOPROPYL-
CYCLOPROPANE, AT 60 MC. IN CCl_4 SOLUTION



No unsaturation was observed in the NMR or in the IR spectra. Most characteristic is a clearly defined doublet (coupling constant 6 cps) centered at $\delta = 0.88$ ppm, assigned to the methyls of an isopropyl group. The doublet character of these two peaks was confirmed by the 100 Mc spectrum. Another sharp signal at $\delta = 0.865$ ppm is superimposed between the two peaks of this doublet. This is interpreted as the center peak of a triplet representing a methyl end group, the outer components of which are barely visible as shoulders. The chemical shift is in very good agreement (8) with values for methyl groups of the type $\text{CH}_3\text{-CH}_2\text{CHRR}'$. The methylene absorption is broadened and centered at 1.2 ppm., partially merged with the very broad band for tertiary hydrogens. The area ratio of CH_3 and $\text{CH}_2 + \text{CH}$ is 1.17, in very close agreement with the calculated value of 1.16 for the tetramer having methyl and isopropyl end groups. All these data are in full agreement with the unrearranged structure (I).



The rearranged polymer (II) would be expected to show an NMR spectrum identical to that obtained from cationically polymerized, rearranged poly-4-methylpentene-1^(b) with a typical singlet for the geminal methyl groups

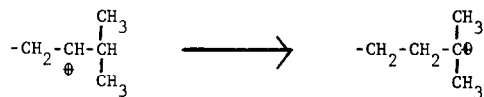


(b) Low temperature cationically polymerized 4-methylpentene-1 was shown to involve hydride shifts which in part converted the secondary carbonium ions initially formed in the propagation steps to the more stable tertiary carbonium ions (9).

at 0.82 ppm. The absence of this, particularly in the 100 Mc spectrum, is taken as evidence that very little, if any rearrangement has taken place during the polymerization of isopropylcyclopropane.

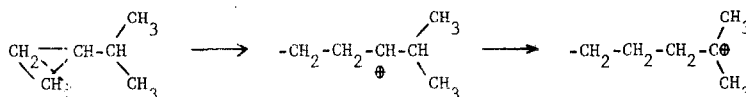
The isopropylcyclopropane polymerizations were carried out in the absence of solvent. Ketley (9b) showed by an infrared study that the degree of rearrangement of the carbonium ion in the case of 4-methylpentene-1 is dependent on the dielectric of the solvent, being greater for alkyl chlorides than for paraffins. In order to eliminate the possibility of a drastic solvent effect in our system, polymerizations of 3-methylbutene-1 were carried out in pentane and in cyclohexane under very similar conditions to those used for isopropylcyclopropane. In agreement with results obtained by Hudson (10), polymers with predominantly rearranged structure containing some unrearranged units were obtained. The amount of unrearranged units is estimated to vary between ca. 5-10% at -30 to -24°C. polymerization temperature to ca. 25% at 0 to 18°C.

When 3-methylbutene-1 is polymerized by Friedel-Crafts catalysts at low temperature, the predominant structure is formed by a 1, 2-hydride shift^(c) (11).



(c) The 3-methyl-2-butyl cation produced in other ways, e.g., in solvolysis or deamination reactions, has been shown to lead, at least in part, to rearranged products (12).

If the cationic polymerization of isopropylcyclopropane were to involve carbonium ions analogous to those formed in olefin polymerizations, it is anticipated that rearrangement would have occurred:



The fact that no appreciable rearrangement was observed is taken as evidence that carbonium ions analogous to those formed from olefins are not involved. (d)

The HF catalyzed alkylation of benzene with isopropylcyclopropane was shown by Pines, Huntsman and Ipatieff to give 2-phenyl-2-methylpentane as the major product (4). Ring opening reactions of isopropylcyclopropane resulting in the formation of carbonium ions may therefore be expected to involve extensive hydride shift to produce the more stable tertiary cation. The alkylation of benzene with other alkyl substituted cyclopropanes such as methyl, ethyl, 1,1-dimethyl, and 1,2-dimethyl leads to products derived from carbonium ions (14). However, alkylation of benzene with cyclopropane itself in the presence of hydrogen fluoride (15), aluminum chloride (16) or sulfuric acid (17) catalysts at low temperatures (0-35°) afforded n-propylbenzene as

(d) It is conceivable that carbonium ions similar to those derived from olefins are formed, but that in the presence of cyclopropane monomer these ions are rapidly converted to π -complexes of the type proposed by Tipper and Walker (2), and that rearrangement by hydride shift is somehow precluded. It is not clear, however, why a cyclopropane should be a more efficient complexing agent for cations than an olefin. We prefer the simple alternative explanation that different types of carbonium ion intermediates are involved in the polymerizations of isopropylcyclopropane and olefins. Perhaps the cationic intermediates involved in the polymerization of isopropylcyclopropane are not completely "open" carbonium ions of the type derived from olefins, but possibly resemble structures analogous to protonated cyclopropanes (13).

the only monoalkylated product. This result implies that under these conditions n-propyl cations were not formed, although they apparently were involved at higher temperatures (65°) with sulfuric acid as catalyst, in which case the product was isopropylbenzene (16a).

The assumption was made above that if carbonium ions were involved in the polymerization of isopropylcyclopropane, the direction of cleavage of the ring would be such that a secondary cation would be initially formed. Cleavage of the ring leading to primary cations is considered unlikely because of energetic considerations, and also because such primary cations would surely rearrange to the more stable secondary or tertiary cations. Rearrangement of primary cations would lead to a CH_3 to $\text{CH}_2 + \text{CH}$ proton ratio close to 3, which is far from the experimental NMR value of 1.17.

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