310. *Preparation and Polymerisation of Some Bicyclic Dienes.*

By (Mrs.) M. A. P. Bowe, R. G. J. Miller, J. B. Rose, and D. G. M. Wood.

The preparation of polymers from four bicyclic monomers, 2,3-dimethylenebicyclo[2,2,1]heptane, 2,3-dimethylene-7-oxabicyclo[2,2,1]heptane, 2,3-dimethylenebicyclo[2,2,2]octane, and 5,6-dimethylenebicyclo[2,2,1]hept-2-ene, is described. The polymers of the first two monomers were amorphous, that of the third crystalline, and the triene gave a cross-linked polymer. Improvements in the published syntheses of the homocyclic monomers, and the preparation of 2,3-dimethylene-7-oxabicyclo[2,2,1]heptane are described.

Polymers of certain cyclic monomers are known in which the rings form part of the polymer chain, for instance, polymers having the repeating units (I) and (II) are obtained by polymerisation of 2,3-dihydrofuran [1] and 1,4-epoxycyclohexane,[2] respectively. Bailey and Golden [3] prepared a crystalline polymer, with a repeating unit (III), from 1,2-dimethylenecyclohexane, and showed that polymerisation of this diene occurred with 100% 1,4-addition. In this polymer chain each C=C group forms part of a ring so that the

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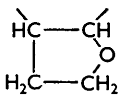
[1] Rose and Barr, *J.*, 1954, 3766.

[2] Wilkins, U.S.P. 2,764,559.

[3] Bailey and Golden, *J. Amer. Chem. Soc.*, 1954, **76**, 5418.

methylene groups must all be *cis*. Bailey and his co-workers[4] have prepared a series of substituted *cis*-1,4-poly-2,3-dimethylenecyclohexanes, all of which are crystalline. The present paper describes the preparation of four similar polymers (from monomers IV—VII) in which the cyclohexane ring is replaced by rigid bicyclic systems. Compounds (IV, VI, and VII) were reported while this work was in progress, but their polymers have not yet been described. Similar preparations of monomers (IV) and (VI) have been reported by Bailey and Lawson[5,6] and by Alder and his co-workers.[7,8] The latter authors have also prepared monomer (VII).[9] The monomer (V), which has not previously been reported, was prepared by the following adaptation of Bailey's general route to cyclic dienes,[10] the compound (VIII) having been prepared by hydrogenation of the Diels–Alder adduct from furan and maleic anhydride. This was reduced with lithium aluminium hydride in boiling tetrahydrofuran, in which the product is readily soluble, so that reduction goes to completion. Difficulties were encountered when ether was used as the reaction medium, for the compound (VIII) is only slightly soluble in this and the lactone (IX) was formed as well as the diol. Bailey and Lawson[5,6] encountered similar difficulties during the preparation of compounds (IV) and (VI), and preferred to reduce the diethyl esters rather than the anhydrides; they did not isolate the lactones. We find that with both bicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride and its bicyclo[2,2,2]octane analogue reduction by lithium aluminium hydride goes to completion in tetrahydrofuran, but that in ether the lactones (X) and (XI) are obtained as well as the diols. The lactones were identified



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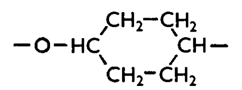

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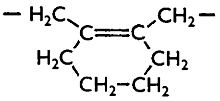

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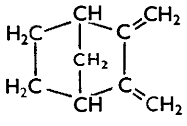

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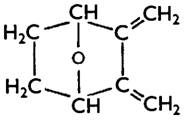
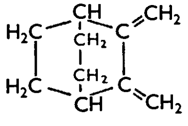


(V)



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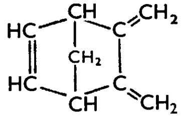

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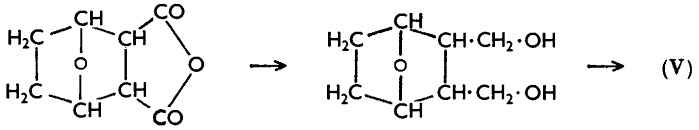

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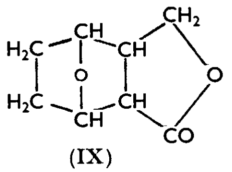

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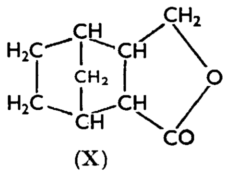
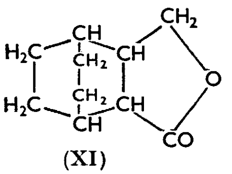


(X)



(XI)

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[4] Bailey, Nat. Acad. Sci., Nat. Res. Council, Bull. 6, No. 370 (1954), p. 113; *Chem. Abs.*, 1956, **50**, 10,691.

[5] Bailey and Lawson, *J. Amer. Chem. Soc.*, 1955, **77**, 1606.

[6] Bailey and Lawson, *J. Amer. Chem. Soc.*, 1957, **79**, 1444.

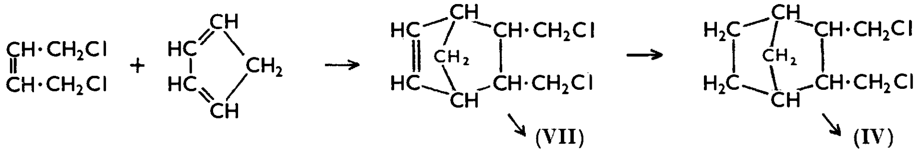
[7] Alder and Roth, *Chem. Ber.*, 1955, **88**, 407.

[8] Alder and Mölls, *Chem. Ber.*, 1956, **89**, 1960.

[9] Alder, Hartung, and Netz, *Chem. Ber.*, 1957, **90**, 1.

[10] Bailey and co-workers, *J. Amer. Chem. Soc.*, 1954, **76**, 2251; 1955, **77**, 990, 1163.

by their infrared absorption spectra which showed bands at 1775 cm.$^{-1}$ characteristic of the carbonyl group in a 5-membered lactone ring,[11] and in the case of (X) by reduction with lithium aluminium hydride in tetrahydrofuran to the diol. The annexed routes to compounds (IV) and (VII) were found to be more convenient than those previously reported. The reaction between cyclopentadiene and 1,4-dichlorobut-2-ene proceeds readily at 200° and, as interconversion between cyclopentadiene and its dimer also occurs at this temperature, dicyclopentadiene can be used directly without prior conversion into the monomeric diene. To prevent side reactions the diene must be treated with two molar equivalents of 1,4-dichloro-2-butene, but the excess of dichloride is easily recovered. Furan and cyclohexadiene do not form adducts with the dichloride at 200°.



All four monomers polymerised readily in emulsion at 50°, a potassium persulphate–dodecanethiol system being used as the catalyst. The polymers of (IV) and (V) were soluble in organic solvents at 20°, the polymer of (VI) was soluble in boiling xylene but was precipitated on cooling, and the polymer of (VII) was completely insoluble. Polymers of (IV), (V), and (VI) were moulded, and threads were drawn from heated mouldings of polymerised (VI); the polymer of (VII) decomposed before softening. All three forms (powder, moulding, and thread) of the polymer of (VI) gave crystalline *X*-ray diffraction patterns. There was a slight amount of planar orientation in the moulding, but no fibre orientation in the thread. The polymers of (IV) and (V) were amorphous and showed no crystalline *X*-ray patterns even after being annealed just below their softening points for several weeks. Some physical properties of the three soluble polymers are tabulated below. Bailey and Lawson [6] claim that the polymer of (IV) is formed with at least 30% 1,2-addition, but they do not describe the polymer or the means used to investigate its structure. However we find that the infrared absorption spectra of these three polymers do not show bands in the region of 883 cm.$^{-1}$ characteristic of the $>C=CH_2$ group. In the case of the homocyclic polymers the sensitivity of the infrared method was measured by means of the reference compound 2-acetoxymethyl-3-methylene[2,2,1]heptane (which absorbs strongly at 883 cm.$^{-1}$) and it was shown that these polymers contained considerably less than one $>C=CH_2$ group per 50 monomer units. Thus if 1,2-addition occurs during polymerisation, then the $>C=CH_2$ groups produced must react further. This, however, would produce an insoluble cross-linked polymer, so that within the limits of detection the infrared evidence indicates polymerisation by 100% 1,4-addition.

Physical properties of the polymers.

Polymer of	n_D^{20}	d	$[\eta]$ (g. dl.$^{-1}$)	Softening point	M. p.
(IV)	1·559	1·055	0·45 *	42°	—
(V)	1·554	1·19	0·33 *	83	—
(VI)	1·582	1·083	0·08 †	141	170—176°

* Measured at 20° in benzene. † Measured at 112° in xylene.

The chain structures of the three soluble polymers are therefore similar, and the marked difference in physical properties between the crystalline polymer of (VI) and the amorphous polymers of (IV) and (V) must be ascribed to structural differences between the individual monomer units. It is generally considered (cf., *e.g.*, Bunn [12]) that a polymer

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[11] Grove and Willis, *J.*, 1951, 877.

[12] Bunn, *J. Appl. Phys.*, 1954, **25**, 820.

can crystallise only if its molecular structure is essentially regular. The polymers of (IV), (V), and (VI) possess regular *chain* structures because, like Bailey's poly-1,2-dimethylenecyclohexanes, they are all *cis*-1,4-diene polymers, but whereas in (VI) the bridged ring is symmetrical this is not the case in (IV) and (V). It is therefore suggested that in (IV) and (V) the marked asymmetry of their bridged ring systems is responsible for the amorphous nature of their polymers. Thus in these latter polymers the bridging groups $-CH_2-$ in (IV) and $-O-$ in (V), will be placed in a random manner on either side of the cyclohexane ring, but this type of asymmetry is not possible in the polymer of (VI) or in Bailey's poly-2,3-dimethylenecyclohexanes.

The polymer of (VII) shows the characteristics of a cross-linked structure, indicating that the endocyclic double bond in the monomer takes part in the polymerisation. Polymerisation would not be expected to occur at the endocyclic double bonds present in the polymers of (IV), (V), and (VI) because of the great steric hindrance afforded by the polymer chain.

EXPERIMENTAL

Preparation of the Monomers.—(a) 2,3-*Dimethylenebicyclo*[2,2,1]*heptane.* Bicyclo[2,2,1]-heptane-2,3-dicarboxylic anhydride was prepared by hydrogenation of the Diels–Alder adduct from cyclopentadiene and maleic anhydride.[13] A slurry of the hydrogenated adduct (1·02 moles) in anhydrous ether (0·50 l.) was added slowly, with stirring, to a mixture of lithium aluminium hydride (1·45 moles) in anhydrous ether (1·5 l.); the mixture was heated under reflux for 8 hr. Then the excess of hydride was destroyed with water, and the calculated quantity of dilute hydrochloric acid was added to decompose the complex. The ether layer was separated, and the aqueous layer extracted continuously with ether, the extract being added to the ether layer. The combined ether extracts were dried (K_2CO_3) and the ether was removed by distillation. After acetic acid and excess of acetic anhydride had been removed from the product obtained by acetylation of the crude diol with acetic anhydride, fractionation of the residue gave two fractions: (1) crude lactone (X), b. p. 140—160°/8 mm., and (2) 2,3-di(acetoxymethyl)-bicyclo[2,2,1]heptane, b. p. 160—161°/8 mm., n_D^{20} 1·4744, m. p. 26—27° (Found: C, 65·0; H, 8·4. Calc. for $C_{13}H_{20}O_4$: C, 64·9; H, 8·3%). Bailey and Lawson [5] report b. p. 145°/4 mm., n_D^{25} 1·4728. The yield of diacetate was 50%. The diol, recrystallised, had m. p. 61—62°; Alder and Roth [7] report m. p. 62°. The diol gave a *dibenzoate*, m. p. 127—129° (Found: C, 75·8; H, 6·6. $C_{23}H_{24}O_4$ requires C, 75·8; H, 6·6%).

2,3-Dimethylenebicyclo[2,2,1]heptane, prepared by pyrolysis of the diacetate as described by Bailey and Lawson,[5] and fractionated, had b. p. 76·0—76·1°/74 mm., n_D^{20} 1·5040 (Found: C, 90·1; H, 10·4. Calc. for C_9H_{12}: C, 90·0; H, 10·0%). Alder and Roth [7] report n_D^{20} 1·5033. The diene gave a Diels–Alder adduct, m. p. 116—118°, with maleic anhydride (Alder and Roth [7] report m. p. 118°). Hydrogenation of the diene in the presence of Adams catalyst (2 mol. absorbed) gave dihydrosantene, b. p. 153°/758 mm., n_D^{20} 1·4611 (Found: C, 86·8; H, 12·9. Calc. for C_9H_{16}: C, 87·0; H, 13·0%) (Alder and Roth [14] give b. p. 150—152°/760 mm., n_D^{20} 1·4636).

The diene was also prepared as follows. A mixture of dicyclopentadiene (1·5 mol.) and 1,4-dichlorobut-2-ene (3 mol.) was heated at 200° for 4 hr. The product gave two main fractions: (1) recovered dichlorobutene, b. p. 53—56°/15 mm., n_D^{20} 1·4899, and (2) 5,6-*di*(*chloromethyl*)*bicyclo*[2,2,1]*hept*-2-*ene*, b. p. 118—122°/15 mm., n_D^{20} 1·5161 (Found: C, 57·2; H, 6·6; Cl, 36·7. $C_9H_{12}Cl_2$ requires C, 56·6; H, 6·3; Cl, 37·2%). The yield of the latter, based on unrecovered dichlorobutene, was 78%. Hydrogenation of this dichloride in the presence of Adams catalyst gave a 76% yield of 2,3-*di*(*chloromethyl*)*bicyclo*[2,2,1]*heptane*, b. p. 123—124°/15 mm., n_D^{20} 1·5111 (Found: C, 55·5; H, 7·8; Cl, 37·1. $C_9H_{14}Cl_2$ requires C, 55·9; H, 7·3; Cl, 36·7%). The saturated dichloride (0·75 mole) was heated under reflux for 40 hr. with potassium hydroxide (2·5 moles) in absolute ethanol (350 ml.). After being diluted with water the product was extracted with light petroleum, and the extract dried ($CaCl_2$). Fractionation gave a 40% yield of 2,3-dimethylenebicyclo[2,2,1]heptane, b. p. 69°/70 mm., n_D^{20} 1·5040.

(b) 5,6-*Dimethylenebicyclo*[2,2,1]*hept*-2-*ene.* Dehydrochlorination of 5,6-di(chloromethyl)-bicyclo[2,2,1]hept-2-ene in a manner analogous to that described for its saturated analogue gave

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[13] Diels and Alder, *Annalen*, 1928, **460**, 113.

[14] Alder and Roth, *Chem. Ber.*, 1954, **87**, 161.

a 42% yield of the triene, b. p. 69·5°/67 mm., n_D^{20} 1·5190 (Found: C, 91·5; H, 8·3. Calc. for C_9H_{10}: C, 91·5; H, 8·5%) (Alder *et al.*[9] report n_D^{20} 1·5180). With maleic anhydride the triene gave an adduct, m. p. 116—122° (decomp.) (lit.,[9] 125°) (Found: C, 72·4; H, 5·8. Calc. for $C_{13}H_{12}O_3$: C, 72·2; H, 5·6%). Hydrogenation of the triene in the presence of Adams catalyst (3 mol. absorbed) gave dihydrosantene, b. p. 153°/758 mm., n_D^{20} 1·4612 (Found: C, 87·3; H, 12·8%).

(c) 2,3-*Dimethylene*-7-*oxabicyclo*[2,2,1]*heptane.* 7-Oxabicyclo[2,2,1]heptane-2,3-dicarboxylic anhydride [15] was made by catalytic hydrogenation in ethyl acetate of the Diels–Alder adduct from furan and maleic anhydride in dioxan.[16] (i) The hydrogenated adduct was reduced with lithium aluminium hydride in ether (method of section a), and the product fractionally crystallised from tetrahydrofuran, giving the crude lactone (IX) (26%), m. p. 118—122°, and 2,3-*di*(*hydroxymethyl*)-7-*oxabicyclo*[2,2,1]*heptane* (74%), purified by sublimation at 80°/10—3 mm., m. p. 58—61° (Found: C, 60·6; H, 9·2. $C_8H_{14}O_3$ requires C, 60·7; H, 8·9%). With acetic acid and acetic anhydride, the diol gave a *diacetate*, m. p. 104—106·5° (Found: C, 59·5; H, 7·45%; sap. equiv., 467. $C_{12}H_{18}O_5$ requires C, 59·5; H, 7·4%; sap. equiv., 462). By other conventional methods the diol gave a *dibenzoate*, m. p. 172—174° (Found: C, 71·7; H, 6·2. $C_{22}H_{22}O_5$ requires C, 72·1; H, 6·0%), and a *di*-p-*nitrobenzoate*, m. p. 182—183·5° (Found: N, 6·2. $C_{22}H_{20}O_9N_2$ requires N, 6·1%). (ii) The hydrogenated adduct (0·41 mole) in tetrahydrofuran (360 ml.) was added to a stirred solution of lithium aluminium hydride (0·73 mole) in tetrahydrofuran (350 ml.) at a rate such as to maintain gentle boiling. The mixture was boiled for 3 hr. and left in the cold overnight. Water (72 ml.) was slowly added with stirring and strong cooling, and the mixture filtered. Almost pure diol (0·193 mole) was obtained by evaporation of the filtrate, and more (0·213 mole) was recovered from the filtration residue by continuous extraction with chloroform. The total yield of diol was 99%. No lactone was found on attempted recrystallisation of the crude product from tetrahydrofuran. 2,3-*Dimethylene*-7-*oxabicyclo*[2,2,1]*heptane*, b. p. 75·5°/36 mm., n_D^{22} 1·5055, d_4^{20} 1·004 (Found: C, 78·6; H, 8·2; hydrogenation equiv., 76. $C_8H_{10}O$ requires C, 78·6; H, 8·2%; hydrogenation equiv., 61), was made by pyrolysis of the diacetate by the method of Bailey and Lawson.[5]

(d) 2,3-*Dimethylenebicyclo*[2,2,2]*octane.* Bicyclo[2,2,2]octane-2,3-dicarboxylic anhydride was prepared by hydrogenation of the Diels–Alder adduct of cyclohexadiene and maleic anhydride.[17] A slurry of the hydrogenated adduct in ether was treated with lithium aluminium hydride, and the product isolated as described in section (a). Fractionation of the crude diol gave crude lactone (XI), b. p. 163—180°/13 mm., and 2,3-di(hydroxymethyl)bicyclo[2,2,2]-octane, b. p. 184—190°/13 mm. On being recrystallised from ether–light petroleum, fraction (2) gave a 36% yield of the pure diol, m. p. 87—88° (Found: C, 70·6; H, 10·5. Calc. for $C_{10}H_{18}O_2$: C, 70·5; H, 10·6%).

This diol was also prepared, in 90% yield, by the method described in section (c, ii). The diol gave a diacetate (60%), b. p. 169°/7 mm., m. p. 24—25° (Found: C, 66·0; H, 8·6. Calc. for $C_{14}H_{22}O_4$: C, 66·0; H, 8·6%). Fractionation of the liquid obtained by pyrolysis of the diacetate at 520—530° with repeated recycling of incompletely pyrolysed material gave a 26% yield of 2,3-dimethylenebicyclo[2,2,2]octane, b. p. 89°/58 mm., n_D^{20} 1·5091 (Found: C, 90·1; H, 9·9. Calc. for $C_{10}H_{14}$: C, 89·5; H, 10·5%) (Alder and Mölls [8] report n_D^{20} 1·5106). With maleic anhydride the diene gave an *adduct*, m. p. 130—132° (Found: C, 72·9; H, 7·1. Calc. for $C_{14}H_{16}O_3$: C, 72·4; H, 6·9%) (lit.,[8] m. p. 132°).

Isolation of the Lactones (IX), (X), *and* (XI).—3-*Hydroxymethylbicyclo*[2,2,1]*heptane*-2-*carboxylic acid lactone*, m. p. 145°, was obtained by recrystallisation (from light petroleum) of the crude material, fraction (1), b. p. 140—160°/8 mm., described in section (a) [Found: C, 70·9; H, 7·7%; *M* (ebullioscopic), 151. $C_9H_{12}O_2$ requires C, 71·0; H, 7·9%; *M*, 152]. Treatment of the lactone (0·10 mole) with lithium aluminium hydride (0·11 mole) in boiling tetrahydrofuran gave an 80% yield of 2,3-di(hydroxymethyl)bicyclo[2,2,1]heptane, m. p. 60—62° (dibenzoate, m. p. 126—128°).

3-*Hydroxymethyl*-7-*oxabicyclo*[2,2,1]*heptane*-2-*carboxylic acid lactone* was obtained as described in section (c) and, purified by recrystallisation from benzene, had m. p. 121—123° (Found: C, 62·9; H, 6·7. $C_8H_{10}O_3$ requires C, 62·4; H, 6·6%).

3-*Hydroxymethylbicyclo*[2,2,2]*octane*-2-*carboxylic acid lactone*, m. p. 136—138°, was obtained

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[15] Diels and Alder, *Chem. Ber.*, 1929, **62**, 554.
[16] Diels and Olson, *J. prakt. Chem.*, 1940, **156**, 285.
[17] Farmer and Warren, *J.*, 1929, 907.

by recrystallisation (from light petroleum) of the crude material, fraction (1), b. p. 163—180°/13 mm., described in section (d) [Found: C, 72·2; H, 8·5%; *M* (ebullioscopic), 171. $C_{10}H_{14}O_2$ requires C, 72·2; H, 8·5%; *M*, 166].

The infrared absorption spectra of the three lactones were recorded on a Hilger H800 double-beam spectrometer as crystalline dispersions in potassium bromide discs. The frequency of the lactone carbonyl absorption band, however, was measured for carbon tetrachloride solutions by comparison with a water-vapour background.

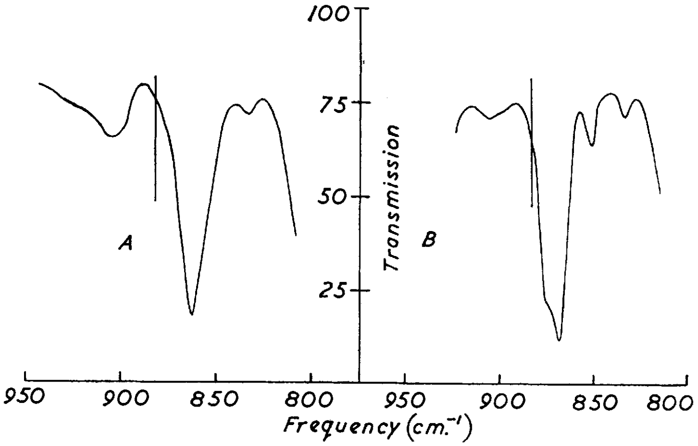

Fig. 1. *Infrared bands of* (*A*) *polymer from* (VI) *and* (*B*) *polymer from* (IV). *The vertical lines are at* 883 *cm.*$^{-1}$.

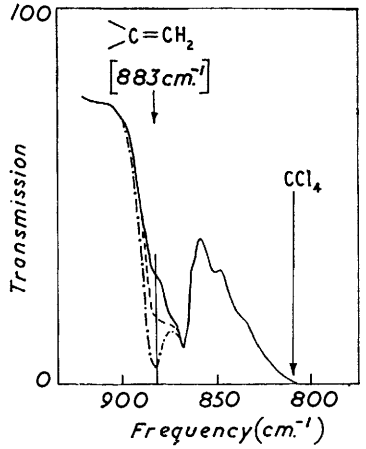

Fig. 2. *Combined spectra of* (———) 2%, (– – – –) 4%, *and* (— · — · —) 10% *v*/*v of* 2-*acetoxymethyl*-3-*methylbicyclo*[2,2,1]*heptane in carbon tetrachloride with the polymer of* (IV).

Polymers.—All four monomers were polymerised in aqueous emulsion at 50° for 15 hr., the following recipe being used: monomer, 5 ml.; water, 9 ml.; sodium oleate, 0·25 g.; dodecane-1-thiol, 0·025 g.; potassium persulphate, 0·015 g. The polymers were coagulated by pouring the emulsions into potassium chloride solution. After being washed free from catalyst residues, the polymers were dried in a vacuum-desiccator. The softening points of moulded samples of each polymer were measured by the " Vicat " method.[18] The m. p. of the polymer of (VI) was measured by means of a hot-stage polarising microscope. The infrared spectra of the three polymers were recorded between 700 and 2000 cm.$^{-1}$, both as dispersions in potassium bromide discs and as heat-pressed films about 0·002 inch in thickness. A spectrum of each polymer has been reproduced for inclusion in the D.M.S. Scheme.

The spectra of the two homocyclic polymers in the 800—950 cm.$^{-1}$ region of the spectrum are shown in Fig. 1 to demonstrate the basis of the statement that the polymers do not show an absorption band at 883 cm.$^{-1}$ where the group $-C{:}CH_2$ was found to absorb. In order to

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[18] See " Kunstharzpresstoffe," W. Hehdorn, V.D.I., Forschungsheft V.D.I.-Verlag G.m.b.H., Berlin, 1934.

investigate the detection limit of this group, solutions of the compound 2-acetoxymethyl-3-methylenebicyclo[2,2,1]heptane were prepared in carbon tetrachloride. The spectra of these were recorded in the 800—950 cm.$^{-1}$ region by placing them together with a film of the polymer at the focus of the sample beam of the spectrometer. The spectral traces obtained from 2%, 4%, and 10% concentrations of the methylene compound, calculated as volume percentages relative to the polymer, are shown in Fig. 2. If the density difference between the monomeric compound and the polymer is neglected, these concentrations represent the molar concentrations of the group $>\mathrm{C{:}CH_2}$ which, if present, in the polymer would produce the spectra shown.

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