The obtained solid product was filtered, dissolved in CF_3COOH, and the polymer was precipitated with MeOH to give 2.5 g (82%) of PMPL-4. The polymer was purified by a double reprecipitation from the CF_3COOH–MeOH system.

CONCLUSIONS

A new complex polyester was obtained by the reaction of α-bromo-methacrylic acid with trialkylamines, which is characterized by the presence of double bonds in the side units of the polymeric chains.

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CYCLOPROPANATION OF OXYGEN-CONTAINING OLEFINS BY A ZINC CARBENOID

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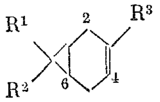
The synthesis of bicyclo[4.1.0]heptene structures with alkyl substituents in the 3 position (I) represents definite difficulties in view of the fact that the usual methods for obtaining similar unsubstituted systems (R^3 = H) by the cyclopropanation of the double bond of 1,4-cyclohexadiene by carbenoid reagents cannot be efficient in the given case, since of the two double bonds of an alkyl-1,4-cyclohexadiene the first to react with the carbenoid will be the alkyl-substituted double bond [1].



(I)

R^1, R^2, R^3 = H or Alk.

It could be expected that the transformation of a substituted double bond to the diol function will permit directing the cyclopropanation in the necessary direction, since it is known that olefins, containing an OH group, easily undergo cyclopropanation, for example, by the zinc carbenoid compounds that are formed from Et_2Zn and alkylidene diiodides [2].

As a model we studied the reaction of 1,2-dihydroxy-1-methyl-4-cyclohexene (II) with Et_2Zn and CH_2I_2. After refluxing the reactants in diisopropyl ether for 20 h the reaction mixture was analyzed by GLC. A comparison with the available samples of the postulated reaction products, namely 3β-4α-dihydroxy-3-methylnorcarane (III) and 3α,4β-dihydroxy-3-methylnorcarane (IV), disclosed that not even traces of bicyclic diols were present in the reaction mixture and, according to the IR spectrum, the starting compound was isolated. As a result, passivation of the double bond of (II) toward a carbenoid reagent is observed in the presence of a diol group.

For the same purpose, namely to direct the cyclopropanation to the unsubstituted double bond, we used the epoxide protection on the example of the reaction of Et_2Zn and CH_2I_2 with 1,2-epoxy-1-methyl-4-cyclohexene (V). Together with cyclopropanation, under the conditions of the given reaction it is possible to have isomerization with a contraction of the six-membered ring, and also the formation of bicyclo[4.1.0]heptane systems with functional substituents in the six-membered ring [3]. A multicomponent mixture of products was obtained, in which, however, one product predominates, which is easily isolated from the reaction mixture by azeotropic distillation with excess CH_2I_2. Its low yield is caused by the fact that the

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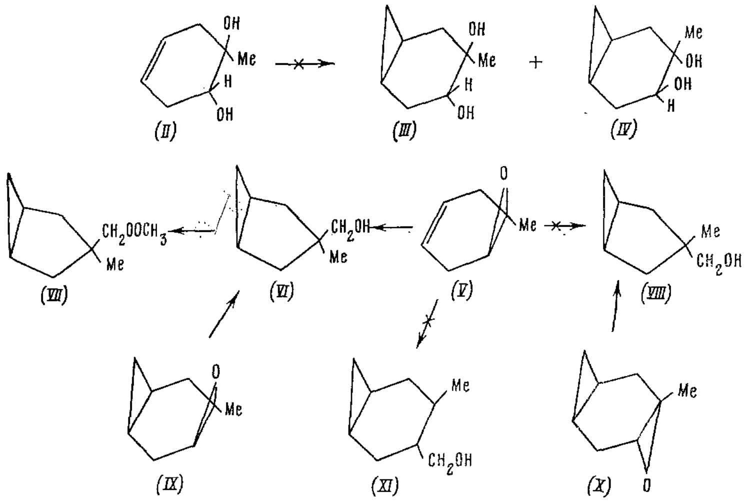

reaction is accompanied by the formation of a viscous mass, apparently of a polymeric character, since it is known that Et_2Zn in combination with various additives initiates the polymerization of epoxides and olefins [4].

The isolated product has a bicyclic structure, which follows from the fact that the PMR spectrum contains the signals of the protons of the cyclopropane ring (CPR) [5], while the alcohol nature of the product is confirmed by the appropriate absorption bands in the IR spectrum. The conclusion that the alcohol has a primary structure follows from the presence of a two-proton singlet signal at 3.18 ppm in the PMR spectrum, which signal corresponds to the protons attached to a carbinol C atom [6]. To confirm the validity of such an assignment we obtained the acetate from the alcohol and compared the PMR spectra of both products, which disclosed that only the singlet, corresponding to the CH_2 group (3.73 ppm), is shifted downfield, which again indicates the primary nature of the acetate substituent and, consequently, the hydroxyl substituent [6].

As a result, on the basis of the spectral characteristics, and also the elemental analysis, it is possible to propose for the product the structure of either the cis- or the trans-3-hydroxymethyl-3-methyl-bicyclo[3.1.0]hexane, i.e. either (VI) or (VIII). The alternate structure of 4-hydroxymethyl-3-methylnorcarane (XI), the product of inserting methylene across the C–O bond, can be excluded on the basis of both the elemental analysis data and the spectral data: the fact that the signals of the CH_3 and CH_2OH groups in the PMR spectrum lack a doublet nature testifies to their location at a tertiary C atom.

The conclusion as to the mutual arrangement of the hydroxymethyl group and the CPR, i.e. the choice between structures (VI) and (VIII), could be made for the isolated alcohol via its counter synthesis from cis-3,4-epoxy-3-methylnorcarane (IX). It proved that both the cis- and the trans-epoxy-3-methylnorcaranes (IX) and (X) under the employed conditions, and using the same ratio of the reactants, react completely. As the TLC analysis disclosed, together with other products, from each epoxide a product is formed whose R_f coincides with that of the alcohol from the cyclopropanation reaction. A comparison of the PMR spectra of these three products disclosed that the spectrum of the alcohol from the reaction with the zinc carbenoid is completely identical with the spectrum of the substance obtained from (IX), while the spectral characteristics of the product from (X), in general being analogous, have certain differences in the chemical shifts of the signals of the CH_3 and CH_2OH groups (0.93 and 1.07 ppm, 3.21 and 3.18 ppm respectively). It may be concluded that we are dealing with stereoisomers (VI) and (VIII). However, the use of only the spectral data to establish the identity of one of the two (VI) and (VIII) samples with the alcohol of the cyclopropanation reaction seemed inadequate in view of their slight differences. The validity of the identification was confirmed by comparing the melting points of the corresponding 3,5-dinitrobenzoates, which for the derivative of the alcohol obtained from (V), and for the 3,5-dinitrobenzoate (3,5-DNB) obtained from (IX), coincided, while their mixed melting point was not depressed.

As a result, the formation of only one isomer (VI) in the reaction of (V) with a zinc carbenoid proves the cis-orienting effect of the epoxide O atom on the cyclopropanation process and testifies to the progress of rearrangement of the formed bicyclo[4.1.0]heptane to a bicyclo[3.1.0]hexane system under the given conditions.

EXPERIMENTAL

The melting points were determined on a Kofler block. The PMR spectra were obtained on a Varian T-60 spectrometer (in CCl_4, and using TMS as the internal standard), and the IR spectra were obtained on a UR-10 instrument. The GLC analysis was run on a Chrom-4 chromatograph, using a 1000 × 3 mm column packed with Tridox deposited on Celite-545. Compound (V) was obtained from 1-methylcyclohexadiene [7] as described in [8]. We used the Noller method [4] to obtain the Et_2Zn. Compounds (IX) and (X) were obtained as described in [5].

trans-1,2-Dihydroxy-1-methyl-4-cyclohexene (II). A mixture of 5.6 g of (V), 120 ml of water, and 5 ml of concentrated H_2SO_4 was stirred for a day at ∿20°C. Then silica gel was added until the entire reaction mass was absorbed. The silica gel was dried as a thin layer in the air, and then the product was eluted with ether. After removal of the solvent the residue was distilled to give 4.6 g of (II) as a viscous liquid with bp 75-80° (2 mm), which crystallized on standing, mp 30°. PMR spectrum (δ, ppm): 1.12 s (CH_3), 3.67 m ($C\underline{H}OH$), 5.48 m (CH=CH). Found: C 65.77; H 9.42%. $C_7H_{12}O_2$. Calculated: C 65.62; H 9.37%.

Reaction of (II) with Et_2Zn and CH_2I_2. To a solution of 1 g of (II) in 30 ml of abs. diisopropyl ether were added from a syringe, in an argon atmosphere, first 1 ml of Et_2Zn and then 4.2 g of CH_2I_2. The reaction mixture was refluxed for 20 h, dilute HCl solution was added, and the mixture was extracted with ether, which was washed in succession with 5% $NaHCO_3$ solution and water, and then dried. After removal of the solvent and separation of the CH_2I_2 at 74-80° (24 mm) the residue, which was distilled using an oil pump, had spectra and R_f values on TLC that were identical with those for (II).

Reaction of 1,2-Epoxy-1-methyl-4-cyclohexene (V) with Et_2Zn and CH_2I_2. To a stirred mixture of 11 g (0.1 mole) of (V) in 50 ml of abs. benzene was added from a syringe, under argon, 10 ml (0.1 mole) of Et_2Zn, after which 42.3 g (0.15 mole) of CH_2I_2 was added dropwise in 1 h at ∿20°, and the mixture was heated for 2 h at 60°. With stirring, the reaction mixture was poured into dilute HCl solution, the organic layer was separated, and the aqueous layer was extracted with ether. The ether extracts were worked up the same as in the preceding experiment. The residue (19.3 g) was distilled and we collected two fractions: 1) 10.3 g with bp 65-69° (18 mm), and 2) 1.3 g with bp 27-55° (2 mm). The residue weighed 8 g. Both fractions were chromatographed on silica gel (eluant = 7:3 petroleum ether—ether) to give 1.4 g of (VI), bp 95-100° (3 mm), n_D^{20} 1.4700. Found: C 75.75; H 11.26%. $C_8H_{14}O$. Calculated: C 76.14; H 11.18%. Infrared spectrum (ν, cm^{-1}): 1040, 1380, 1410, 2830, 2900, 2990, 3320. PMR spectrum (δ, ppm): 0.07 m and 0.7 m (CH_2 in CPR), 107 s (CH_3), 3.18 ($C\underline{H}_2OH$), 3.5-DNB, mp 79-81°.

Acetate of cis-3-Hydroxymethyl-3-methylbicyclo[3.1.0]hexane (VIII). To 0.15 g of (VI) in 3 ml of abs. pyridine was added 0.5 ml of Ac_2O. The mixture was kept at ∿20° for a day, diluted with water, and extracted with ether. The extract was washed in succession with dilute HCl solution and water, and then dried over $MgSO_4$. After removal of the solvent the residue (0.13 g) was distilled, bp 100-105° (4 mm), n_D^{20} 1.4560. Found: C 71.78; H 10.00%. $C_{10}H_{16}O_2$. Calculated: C 71.39; H 9.59%. Infrared spectrum (ν, cm^{-1}): 1740. PMR spectrum (δ, ppm): 0.08 m and 0.70 m (CH_2 in CPR), 1.13 s (CH_3), 2.03 s (CH_3OCO) 3.73 s ($C\underline{H}_2OCOCH_3$).

Reaction of trans-3,4-Epoxy-3-methylnorcarane (X) with Et_2Zn and CH_2I_2. To a stirred solution of 0.55 g of (X) in 100 ml of abs. benzene were added in an argon stream first 1 ml of Et_2Zn and then 2.6 g of CH_2I_2, after which the mixture was kept for 3 h at 70°. It was worked up the same as described above. The reaction mixture was chromatographed on silica gel to give 0.08 g of (VIII). PMR spectrum (δ, ppm): 0.07 m and 0.67 m (CH_2 in CPR), 0.93 s (CH_3), 3.21 s ($C\underline{H}_2OH$). 3,5-DNB, bp 100-101°. Found: C 56.61; H 5.16; N 8.43%. $C_{15}H_{16}N_2O_6$. Calculated: C 56.26; H 5.04; N 8.74%.

Reaction of cis-3,4-Epoxy-3-methylnorcarane (IX) with Et_2Zn and CH_2I_2. The reaction conditions and workup were the same as in the preceding experiment. We isolated (VI) by chromatography on silica gel. 3,5-DNB, mp 78-80°.

CONCLUSIONS

When 1,2-dihydroxy-1-methyl-4-cyclohexene is reacted with Et_2Zn and CH_2I_2 the diol group inhibits reaction at the double bond, while the epoxide function in 1,2-epoxy-1-methyl-4-cyclohexene exerts a cis-orienting effect on the cyclopropanation process, which is accompanied by isomerization of the bicyclo[4.1.0]heptane system to the bicyclo[3.1.0]hexane sytem.

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BEHAVIOR OF OCTAMETHYLBIPHENYLENE IN STRONGLY ACID MEDIA

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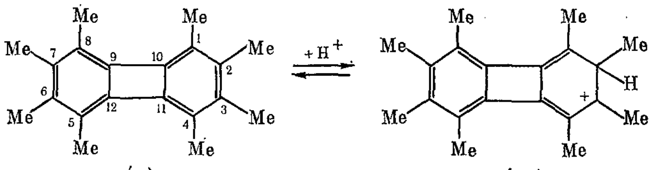
547.678

As a continuation of studying the effect of substituents in the biphenylene molecule on the isomeric composition, and on the rearrangement direction and rate of the corresponding arenonium ions [1], we studied the ions that are generated from octamethylbiphenylene (I). It is possible to consider the 2-H-1,2,3,4,5,6,7,8-octamethylbiphenylenonium ion (II) as a precursor of this series of cations, which apparently should be formed by the protonation of (I) [1, 2].



(I)
(II)

However, ion (II) is formed in negligible amounts when (I) is reacted with trifluoroacetic acid; the formation of the (I) cation-radical was recorded by the NMR and EPR methods [3].

We established that in more acid media [HSO_3F, HSO_3F-SO_2ClF (1:5)*, $CF_3SO_3H-SO_2ClF$ (1:2), and $HCl-Al_2Cl_6-CH_2Cl_2$] the octamethylbiphenylene (I) is protonated to give ion (II), whose structure was established by the ^1H (Fig. 1, Table 1) and ^{13}C NMR methods: (HSO_3F-SO_2ClF (1:5)), −70°: 208.7 (C^3), 194.1 (C^{11}), 157.2 (C^1), 155.3 (C^9), 141.9 (C^4 or C^7), 141.0 (C^{12} or C^{10}), 139.7 (C^5, C^7 or C^4), 138.8 (C^{10} or C^{12}), 130.2 (C^6 or C^8), 129.1 (C^8 or C^6), 54.5 (C^2), 25.0, 20.9, 17.8, 17.2, 16.8, 15.9, 15.4, 14.2 ppm (CH_3 groups) (cf. [1]).

In the PMR spectrum of a solution of (I) in HSO_3F-SO_2ClF (1:5), prepared at −120°, is observed, together with the signals of ion (II), a singlet at 7.6 τ($\nu_{1/2} \approx 20$ Hz), which, when the temperature is raised, undergoes a very strong broadening clear up to its disappearance at −80°, in which connection the observed changes are reversible. A further increase in the temperature of the solution up to −40° leads to an irreversible broadening of the signals. A similar change is also observed for solutions in HSO_3F and $CF_3SO_3F-SO_2ClF$ (at −20°). It is probable that the indicated temperature changes testify to the progress of processes that are related to the formation of cation-radical particles [3].

In the PMR spectrum of ion (II), generated in the $HCl-Al_2Cl_6-CH_2Cl_2$ system, new signals appear when the temperature is raised to −20°, which testify to the instability of cation

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*The acid:diluent volume ratio is indicated here and subsequently.

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