ORGANIC CHEMISTRY

REACTION OF UNSATURATED COMPOUNDS WITH DIAZOALKANES.

COMMUNICATION 3. CYCLOPROPANATION OF CYCLOOCTATETRAENE WITH DIAZOMETHANE*

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One of the most convenient methods for the production of cyclopropane compounds is catalytic reaction of olefins with diazomethane. In the presence of compounds of Cu(I), diazomethane cyclopropanates practically any double bonds in mono- and polyolefins [2, 3], while the degree of transformation of double bonds with various structures into cyclopropane fragments depends on the tendency of these double bonds to form π-olefin complexes with the catalyst. Here the side reactions of the initial olefins are eliminated almost completely, and this makes it possible to use this method successfully for the cyclopropanation of reactive olefins.

One of the interesting subjects for cyclopropanation with diazomethane is the highly unsaturated hydrocarbon 1,3,5,7-cyclooctatetraene (COT). Only the products from the mono- and dicyclopropanation of COT have been described in the literature. The first of them, bicyclo[6.1.0]nona-2,4,6-triene (I), has been synthesized by several methods and, in particular, by the reaction of methylene iodide with COT in the presence of a Zn/Cu couple [4] and by the reaction of diazomethane with COT in the presence of cuprous chloride [5] with yields of 5.5 and 25-30%, respectively. With diazomethane and cuprous chloride as catalysts the double cyclopropanation products cis-tricyclo[7.1.0.0^{4,6}]deca-2,7-diene (IIa) and tricyclo-[7.1.0.0^{2,4}]deca-5,7-diene (III) with unestablished configuration for the cyclopropane fragments were also obtained from COT [6]. The formation of trans-tricyclo[7.1.0.0^{4,6}]deca-2,7-diene (IIb) was observed during the thermal isomerization of pentacyclo[5.3.0.0^{2,6}0^{3,5}.0^{8,10}] at 150°C [7]. As established, conformational inversion of the eight-membered ring takes place comparatively readily in the given isomer.

In the present work we studied the catalytic reaction of COT with diazomethane with the reagents in various ratios and tried to identify all the products formed by cyclopropanation of COT. The experiments were carried out at −10 to 0°C by passing diazomethane, diluted with an inert gas (nitrogen or argon), into a solution of COT and methylene chloride (about 1:1 by volume) containing about 5 mole % of cuprous chloride. As expected, all the possible products from the cyclopropanation of COT appear under such conditions. Here the formation of the products from more extensive cyclopropanation increases with the addition of diazomethane. Thus, with a COT—diazomethane ratio of 1:1-1.2 the reaction mixture contains about 44% of bicyclononatriene (I), 14% of tricyclodecadienes (II) and (III), and about 5% of triple cyclopropanation products (IV). However, with a COT—diazomethane ratio of 1:3 the mixture contains up to 36% of tetracyclo[8.1.0.0^{2,4}.0^{5,7}] undecenes (IV) and 15-17% of pentacyclo-[9.1.0.0^{2,4}.0^{5,7}.0^{8,10}]dodecanes (V) in addition to compounds (I-III). It should be noted that after the addition of 1-1.3 mole of diazomethane calculated for 1 mole of COT the reaction mass begins to darken as a result of the formation of metallic copper, and the cyclopropanation is greatly retarded. In order to continue successful cyclopropanation in accordance with our previously proposed scheme of catalytic cyclopropanation of olefins with diazomethane [3] we filtered the reaction mixture under argon and added a fresh portion of cuprous chloride (see scheme on following page).

The structures of the hydrocarbons (I-V), which were enriched in the main component to 85-97% by high-performance vacuum rectification and preparative GLC, were established on the basis of the high-resolution PMR spectra. As known [8], the triene (I) isomerizes comparatively readily at 90°C to 8,9-dihydroindene. We did not therefore try to isolate it, but the formation of (I) was confirmed by recording the PMR spectrum of the reaction mixture ob-

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*For Communication 2, see [1].

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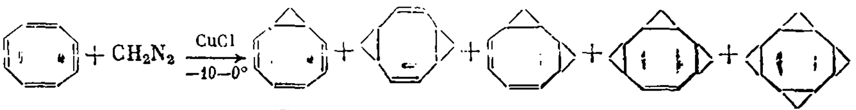


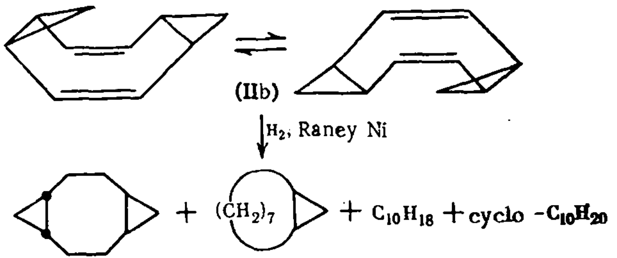
	(I)	(II)	(III)	(IV)	(V)
1 : 1	44%	6%	8%	5%	1–2%
1 : 3	13%	12%	14%	36%	15–17%

tained with a small degree of conversion of the COT (about 30%). Under these conditions the degree of formation of the double cyclopropanation products was still fairly small, but the initial COT, which gives a singlet at δ 5.79 ppm, does not interfere with the interpretation of the spectrum of (I).

Among the double cyclopropanation products the simplest spectrum (Table 1) corresponds to the symmetric molecule of (IIa), which evidently exists preferentially in the "boat" form with two condensed exo-cyclopropane fragments. The isomeric hydrocarbon (IIb) has the longest retention time (GLC, SE-30) among the double cyclopropanation products, and its PMR spectrum is characterized by a set of several strongly broadened signals. Hydrogenation of (IIb) over Raney nickel at a hydrogen pressure of 80 atm and at 60-70°C leads to a mixture of hydrocarbons, in contast to (IIa), which mainly gives cis-tricyclo[7.1.0.0^{4,6}]decane (VI). According to the PMR spectrum [9], the main component of this mixture was bicyclo[7.1.0]decane, formed as a result of the opening of one of the cyclopropane fragments. Such isomerization is evidently due to the additional strains in the molecule arising from inversion of the eight-membered ring and preferential initial hydrogenation of one of the intracyclic bonds.

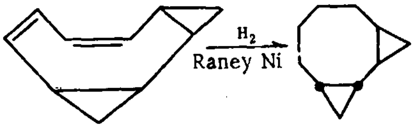
The diene (III) is the trans isomers (IIIa), as confirmed by its hydrogenation under analogous conditions to the known trans-tricyclo[7.1.0.0^{2,4}]decane (VII); it was not possible to detect the cis isomer (IIIb). At the same time, during the isolation of (IIa) both by fractional distillation and by preparative GLC the isomeric hydrocarbon without the cyclopropane fragments was always detected. Its PMR spectrum contains a set of signals in the region of 5.6-6.0 ppm and an unresolved signal at δ 2-2.2 ppm with equal intensity for these two groups of signals. According to [10], this unsaturated hydrocarbon is trans-1,4,9,10-tetrahydronaphthalene (VIII), which is probably formed by the isomerization of cis-(IIIb). Analysis of the PMR spectrum of the reaction mixture showed that the triene (VIII) is present in the initial mixture but does not appear from (IIa), (IIb), or (IIIa) during their isolation. The (IIa):(IIb):(IIIa):(VIII) ratios in the mixture obtained by the passage of two moles of diazomethane into one mole of COT in methylene chloride amount to ~2:1.5:5:1.

(IIa) (VI), 90%

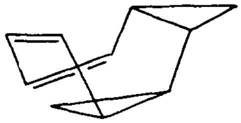


(IIb)

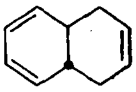
10-12% 65-70% 15-18% ~5%



(IIIa) (VII), 90%

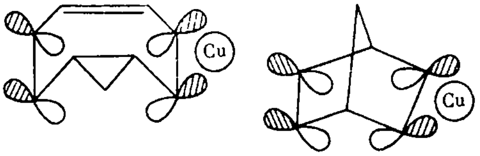


(IIIb)



(VIII)

Thus, the further cyclopropanation of (I) by diazomethane in the presence of cuprous chloride is nonstereoselective. Unlike the cyclopropanation of 1,5-cyclooctadiene (COD) [3], where the corresponding cis- and trans-tricyclodecanes are formed in an approximately equal ratio, the present reaction involves the preferential formation of adducts with the exo configuration in the cyclopropane fragments. The conjugated system of double bonds in the eight-membered ring evidently fixes it in the "boat" form, as a result of which the double bonds are similar in character to the double bonds in norbornadiene. This leads to preferred complex formation between these bonds and the cuprous chloride on the side with least steric hindrances and subsequent cyclopropanation by diazomethane to form the adducts with the exo orientation of the cyclopropane fragments



The products from triple cyclopropanation of COT are formed as the three possible isomers, among which the unsymmetrical isomer (IVc) is readily isolated both by preparative GLC and by vacuum rectification. The other two isomers (IVa) and (IVb) have very similar boiling points, but (IVa) crystallizes out from the mixture at −5 to 0°C.

The (IVa):(IVb):(IVc) ratios in the reaction mixture amount to 1.1:0.3:1. The PMR spectra of all the obtained tetracycloundecenes (IV) have a characteristic set of signals corresponding to the protons of two or three exo-cyclopropane fragments (Table 1). However, the signals of the syn- and anti-methylene protons in the endo-cyclopropane fragments (IVb) and (IVc) change places, and the signal for the H^e proton in the trans position to the methine protons of this cyclopropane fragment becomes downfield (J_{trans} = 5-5.5 Hz). In addition, the two methylene protons H^e and H^f in (IVb) have a small spin–spin coupling constant (J ~ 0.6 Hz) due to their coupling with the H^c protons.

By virtue of the nonequivalence of all the protons the isomer (IVc) has the largest number of signals in the PMR spectrum. Since some of the signals have approximately the same multiplicity or overlap in pairs, the double resonance method was used for their assignment. This made it possible also to establish that the angular protons in the oriented endo-cyclopropane fragment have a downfield shift compared with the corresponding protons in the exo-cyclopropane fragments (Table 1).

In order to confirm the structure of the obtained hydrocarbons, we studied the cyclopropanation of (IIa) and (IIb) with diazomethane under the same conditions. Here compounds (IVa) and (Va) were obtained preferentially from (IIa), and the isomer (IVc) and the corresponding product from total cyclopropanation (Vb) and a small amount, evidently, of (Vc) were obtained from (IIb). The results show that the cyclopropanation of the dienes (II) and also of the olefins formed from them is even more stereoselective than that of the triene (I) and leads to the preferential formation of the corresponding homocyclooctatetraenes with the exo-oriented cyclopropane fragments in the molecule. In addition, the formation of the hydrocarbons (IVa) and (IVb) in a ratio of 10:1 from (IIa) does not agree with their ratio in the

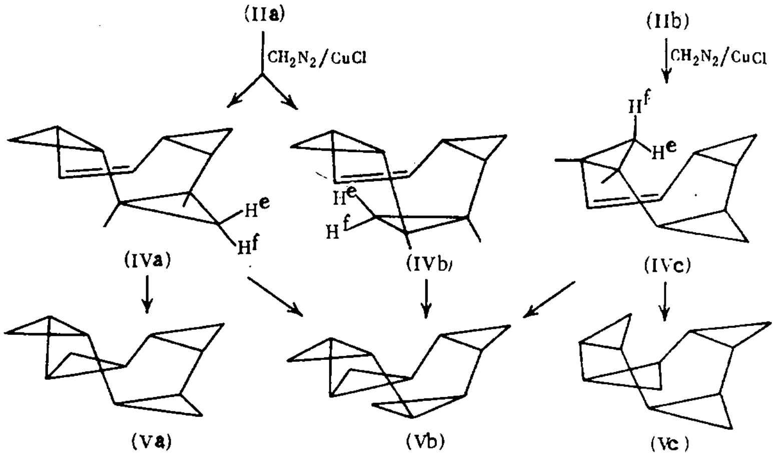
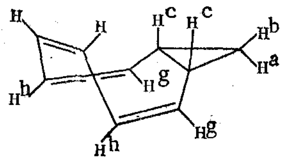
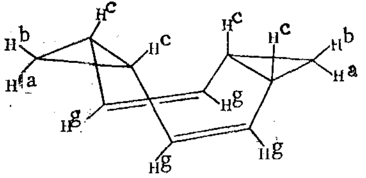
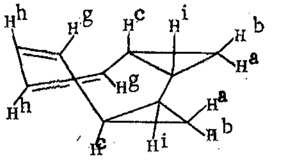
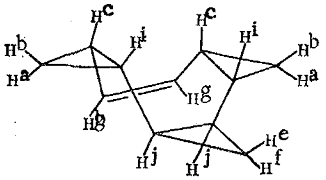
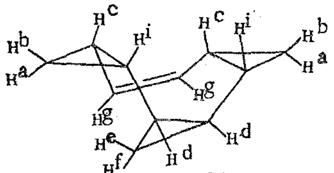
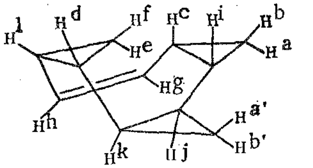
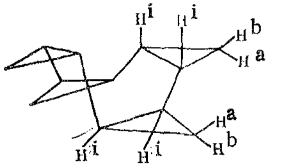
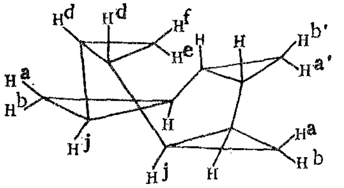


TABLE 1. PMR Spectra of the Homocyclooctatetraenes (I-V) in Deuterochloroform (δ, ppm; J, Hz)

Compound	H^a, $H^{a'}$	H^b, $H^{b'}$	H^c, H^m	H^d	H^e	H^f	H^g	H^h	Other protons
 (I)	0,05 dt J_{ab}=3,5 J_{ac}=6,0	1,02 dt * J_{ab}=3,5 J_{bc}=9,0	1,42 dd * J_{ac}=6,0 J_{bc}=9,0 J_{cg}<1				5,96 bd J_{gh}=11,0	6,03 dt J_{gh}=11,0 J=1,0	5,90 nm
 (IIa)	0,09 dt J_{ab}=4,2 J_{ac}=6,3	0,91 dt J_{ab}=4,2 J_{bc}=8,7	1,68 bdd J_{ac}=6,3 J_{bc}=8,7				5,52 bs		
 (IIIa)	0,11 ddd J_{ab}=4,3 J_{ac}=6,3 J_{ai}=5,2	1,0 dt J_{ab}=4,3 $J_{bc}\sim J_{bi}$ = =8,5	1,39 m				5,41 dd * J_{gh}=9,5 J_{cg}=2,0	6,02 bd J_{gh}=9,5	0,45 m (Hi)
 (IVa)	0,19 ddd J_{ab}=4,3 J_{ac}=6,2 J_{ai}=5,0	1,0 dt J_{ab}=4,3 $J_{bc}\sim J_{bi}$ = =8,4	1,40 m		0,22 dt J_{ef}=4,5 J_{ej}=5,2	0,90 dt J_{ef}=4,5 J_{fj}=8,6	5,74 bs		0,83† (Hi) 0,28 m (Hj)

 (IVb)	0,05 ddd $J_{ab}=3,8$ $J_{ac}=6,2$ $J_{ai}=7,1$	0,81 ddd $J_{ab}=3,8$ $J_{bc}=8,1$ $J_{bi}=9,0$	1,48 m	1,37†	0,74 dt * $J_{ef}=4,8$ $J_{ed}=5,0$ $J_{ce}=0,7$	−0,17 dt * $J_{ef}=4,8$ $J_{df}=9,4$ $J_{ef}=0,5$	5,75 bs		1,26 m (Hi)
 (IVc)	0,15 m 0,17 at‡ $J_{gem}=3,8$ $J_{trans}=6,4$	1,07 dt, 0,86 dt $J_{gem}=3,8$ $J_{cis}=8,8$	1,22 m 1,38 ddt $J_{dl}\sim J_{fl}==8,9$ $J_{el}=5,6$ $J_{hl}=6,4$	1,61 ddt $J_{de}=5,6$ $J_{dk}=3,0$ $J_{dl}\sim J_{df}==8,9$	1,94 dt $J_{ef}=5,0$ $J_{de}\sim J_{el}==5,6$	0,54 dt $J_{ef}=5,0$ $J_{df}\sim J_{fl}==9,0$	5,46 dd $J_{gh}=11,2$ $J_{ch}=2,2$	5,99 ddd $J_{gh}=11,2$ $J_{hl}=6,4$ $J_{ch}=2,5$	0,40 ddt (Hi) $J_{ai}=5,2$ $J_{ij}=6,3$ $J_{bi}\sim J_{ci}==8,8$ 0,92 m and 0,98 m (H^j) and (H^k) †
 (Va)	0,24 bdt $J_{ab}\sim4,3$ $J_{ai}\sim5,5$	0,99 bdt $J_{ab}\sim4,3$ $J_{bi}\sim8,2$							0,40 bdd (H^i) $J_{ai}\sim5,5$ $J_{bi}\sim8,2$
 (Vb)	0,19 m†	0,92 dt and 1,22 dt $J_{gem}\sim4,0$ $J_{cis}\sim8,2$		1,40 bdd $J_{de}\sim5,2$ $J_{df}\sim9,0$	1,13 g* $J_{de}\sim J_{ef}==5,2$	−0,06 dt $J_{ef}=5,2$ $J_{df}=9,0$			0,38 m† (4H) 1,06 m (H^j)

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*Each line of the given signal is split into a triplet with J = 0.4-0.7 Hz.
†The proton signals overlap with the other signals or form a closely coupled system of protons.
‡The signals of the respective protons become well resolved when the spectrum is recorded in deuter0 benzene: Δδ = 0.09 ppm.

reaction mixture obtained during the cyclopropanation of COT and equal to 3-3.5:1. The precursor of (IVb) is evidently the conjugated diene (IIIb), since neither (IIb) nor (IIIa) can give the isomer (IVb). Thus, the isomer (IIIb) is in fact formed in addition to other dienes in the cyclopropanation of COT, and its isomerization to (VIII) under the reaction conditions (≤0°) takes place fairly slowly.

Among the products from exhaustive cyclopropanation of COT the main products are the isomers (Va) and (Vb), which also have the preferred exo orientation of the cyclopropane fragments in the molecule. The more symmetrical isomer (Va) crystallizes out from the residue obtained after the isolation of the preceding homocyclooctatetraenes (I-IV) and melts at 104-107°C.

The use of palladium compounds, including the norbornadiene complex of Pd(0) as catalyst for the cyclopropanation of COT was unsuccessful. In all the experiments the solution acquired an intense red-brown color, but the COT remained unchanged. In this case the formation of Pd(II) cyclooctatetraenide through conversion of the cyclooctatetraene system into an aromatic dianion is evidently possible.

EXPERIMENTAL

The reaction mixtures were analyzed by GLC on an LKhM-8MD (V) chromatograph with a flame-ionization detector and an I-02 integrator (300 × 0.3 cm columns with 5% silicone SE-30 or 10% Carbowax 20M on Chromaton N-AW-DMCS, helium, 30 ml/min). Preparative separation was realized on an LKhP-71 chromatograph (150 × 1.2 cm column with 5% silicone SE-30 on Chromaton N-AW-DMCS, 0.25-0.36 mm, nitrogen, 220 ml/min) and on an automatic Fischer HMS-500A fractionating column. The PMR spectra were obtained on a Bruker WM-250 spectrometer at 250 MHz for 5-8% solutions in deuterochloroform with TMS as internal standard. The cyclooctatetraene (COT) was distilled under vacuum before use. The diazomethane was obtained by alkaline hydrolysis of N-nitrosomethylurea (NMU), and cyclopropanation was realized according to [3].

Cyclopropanation of COT. To a solution of 5.2 g (0.05 mole) of COT in 5 ml of methylene chloride was added 0.2-0.3 g of cuprous chloride. Diazomethane, diluted with argon in a ratio of about 1:5 was passed at −10 to 0°C. After the addition of 10-11 g of NMU, which corresponds to the passage of an average of 0.06 mole of diazomethane, the darkened reaction mixture was filtered under argon through a dense filter, a further 0.1-0.2 g of cuprous chloride was added, and cyclopropanation was continued. When a threefold molar quantity of diazomethane had been passed (about 25 g of NMU), the reaction mixture was diluted with 20 ml of pentane and filtered through a small layer of silica gel. The solvents were distilled, and the slightly yellowish residue, obtained from two analogous experiments (total weight about 14 g), was submitted to fractional distillation under vacuum. The predistillate (1.6 g) boiling up to 85°C (60 mm Hg) consisted mainly of cis-8,9-dihydroindene in a mixture with its trans isomer [9] and the initial COT; the fraction boiling at 93-94°C (40 mm Hg) (yield 0.9 g) was a mixture of 1,4,9,10-tetrahydronaphthalene (VIII) of cis-tricyclo[7.1.0.$0^{4,6}$]deca-2,7-diene (IIa) in a ratio of ~2.2:1; the fraction boiling at 94-95.1°C (40 mm Hg) (yield 0.9 g) was also a mixture of (VIII) and (IIa) but in a ratio of 1:2.8 and with a small amount of (IIIa) (~5%) as impurity. The yield of (IIa) was ~7%, and the yield of (VIII) was 6%. All the intermediate fractions, collected in amounts of 0.2-0.3 g, were mixtures of the respective hydrocarbons. The yields of each of the components are given with due regard to their contents in the intermediate fractions.

PMR spectrum of (VIII) (δ, ppm): 5.98 m (2H), 5.76 m (2H), 5.71 dd (2H, J = 7 and 3 Hz), 2.26 m (4H), 2.1 m (2H). On storage compound (VIII) is oxidized and/or oligomerized more rapidly than (IIa). The diene (IIa) can therefore be obtained with purity of up to 95% by repeated vacuum distillation.

Further fractional distillation of the reaction mixture gave 1.6 g (13%) of trans-tricyclo[7.1.0.$0^{2,4}$]deca-5,7-diene (IIIa) with 5-7% of (IIa) as impurity [bp 104.8-105.6°C (40 mm Hg)] and 0.5 g (about 5%) of trans-tricyclo[8.1.0.$0^{2,4}$.$0^{5,7}$]deca-2,7-diene (IIb) [bp 104.8-105.6°C (40 mm Hg)]. PMR spectrum (δ, ppm): broad signals at 5.6, 2.2, 1.6, 1.0, and 0.1 ppm with integral intensities of 4:1:4:2:1. By subsequent fractional distillation 0.5 g (about 5%) of cis,cis-tetracyclo[8.1.0.$0^{2,4}$.$0^{5,7}$][undec-8-ene (IVb) was obtained with 12-15% of the isomer (IVa) as impurity; bp 118-119°C (36 mm Hg) and also 2.2 g (18%) of trans, cis-tetracyclo[8.1.0.$0^{2,4}$.$0^{5,7}$]undec-8-ene (IVa) with 8-10% of the isomer (IVb) as impurity; bp 118-119°C (36 mm Hg). From the last fraction by the addition of 2 ml of hexane at −5°C the isomer (IVa) was isolated with a purity of about 97%; mp 9-10°C. The fraction boiling at 118-119°C (36 mm Hg) represented trans,trans-tetracyclo[8.1.0.0^{2,4}.0^{5,7}]undec-8-ene (IVc); 2.0 g (15%). From the distillation residue after the addition of a small amount of hexane 0.8 g (about 7%) of trans,cis,trans-pentacyclo[9.1.0.0^{2,4}.0^{5,7}.0^{8,10}] dodecane (Va) was isolated in the form of colorless crystals; mp 104-107°C. From the filtrate after removal of the hexane and distillation 1.55 g (10%) of a colorless liquid was obtained, boiling at 88-95°C (4 mm Hg) and containing 80-85% of cis,cis,trans-pentacyclo[9.1.0.0^{2,4}.0^{5,7}.0^{8,10}]dodecane (Vb), 11-13% of the isomer (Va), and evidently a small amount of the trans,trans,cis-pentacyclododecane (Vc).

The dienes (IIa) and (IIb) were cyclopropanated similarly in the presence of cuprous chloride with an equimolar amount of diazomethane. From (IIa) under these conditions (IVa) and (IVb) were obtained in a ratio of about 10:1 (overall yield 43%) and (Va) (yield 20%). From (IIb) (IVc) (yield 45%) and also (Vb) and (Vc) were obtained in a ratio of about 7:1 (overall yield 20%).

Hydrogenation of trans-Tricyclo[7.1.0.0^{4,6}]deca-2,7-diene (IIb). In an autoclave we placed 0.5 g of (IIb), 4.5 ml of hexane, and 0.3-0.4 g of Raney nickel. The mixture was agitated at 60°C and a hydrogen pressure of about 80 atm for 1 h. According to chromato-mass spectrometry, the obtained hydrogenation product contained not less than six components, for two of which $M^+ = 136$ and 140 and for the others $M^+ = 138$. The main component of the mixture (65-70%), isolated by preparative GLC (150°C), corresponded to bicyclo[7.1.0]decane. PMR spectrum (δ, ppm: 1.97 m, 1.78 m, 1.3-1.65 m, 0.98 m (12 H, $6CH_2$), 0.76 m (2H, HC—CH), 0.51 ddd (1H, H-anti, $J_{gem} = 4.6$, $J_{cis} = 7.6$ and 8.8 Hz), −0.41 dt (1H, H-syn, $J_{gem} = 4.6$, $J_{trans} = 5.5$ Hz). The PMR spectrum of the reaction mixture also contained signals which coincided fully with the corresponding signals of the crystalline trans isomer of tricyclo[7.1.0.0^{4,6}]-decane, formed at the rate of 10-12% (δ, ppm): 2.18 m (4H, 2HC—CH), 0.7-0.95 m (8H, $4CH_2$), 0.56 dt (2H, H-anti, $J_{gem} = 4.2$, $J_{cis} = 7.6$ Hz), −0.16 dt (2H, H-syn, $J_{gem} = 4.2$, $J_{trans} = 4.8$ Hz). In addition, the spectrum contained a narrow singlet at 1.5 ppm, which evidently corresponds to cyclodecane.

cis-Tricyclo[7.1.0.0^{4,6}]decane (VI). By the hydrogenation of the diene (IIa) under similar conditions cis-tricyclodecane (VI) was obtained with a yield of about 90% and identical with the corresponding isomer obtained earlier [3]. PMR spectrum (δ, ppm): 2.06 m (4H, $2CH_2$), 1.16 m (4H, HCCH), 0.88 m (4H, $2CH_2$), 0.64 dt (2H, H-anti, $J_{gem} = 4.2$, $J_{cis} = 7.6$ Hz), −0.22 dt (2H, H-syn, $J_{gem} = 4.2$, $J_{trans} = 4.6$ Hz).

trans-Tricyclo[7.1.0.0^{2,4}]decane (VII). trans-Tricyclodecane (VII) was obtained similarly with the yield of about 90% by the hydrogenation of the diene (IIIa). PMR spectrum (δ, ppm): 2.1 m, 1.82 m, 1.2 m (6H, $3CH_2$), 0.85 m (4H, CH_2 and H-anti), 0.55 m and 0.42 m (4H, HCCH), −0.08 dt (2H, H-syn, $J_{gem} = 4.0$, $J_{trans} = 4.7$ Hz).

CONCLUSIONS

The cyclopropanation of the double bonds in cyclooctatetraene by diazomethane in the presence of cuprous chloride is nonregioselective and leads to the formation of the corresponding mono-, di-, tri-, and tetracyclopropanation products with yields determined by the amount of added diazomethane. The obtained bis-, tris-, and tetrakishomocyclooctatetraenes are characterized by a preference for the isomers with the exo orientation of the cyclopropane fragments.

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OXIDATIVE CLEAVAGE OF CYCLOALKANONES BY HYDROGEN PEROXIDE

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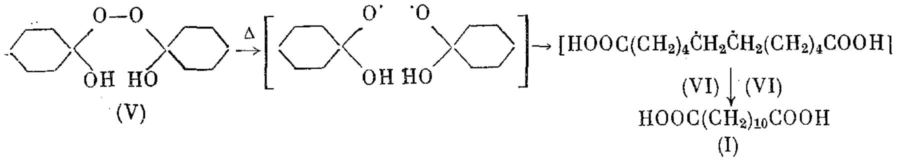
Cycloalkanones react with aqueous solutions of hydrogen peroxide at about 20°C to give complex mixtures of peroxides which are in equilibrium with themselves and with the starting materials [1-3]. The principal factor determining the composition of the mixture is the pH of the solution. Under neutral conditions, a mixture of adducts is obtained consisting of the α-hydroxycycloalkyl hydroperoxide, α,α'-dihydroxydicycloalkyl peroxide, and α-hydroxy-α'-hydroperoxydicycloalkyl peroxide [1]. In acidic media ($HClO_4$, acetic acid), cyclic cycloalkanone di- and triperoxides are obtained [2]. Oxidation of cycloalkanones with hydrogen peroxide at 40-70°C in acetic acid gives lactones [4]. There is, however, little information in the literature on the reactions of cycloalkanones with hydrogen peroxide at higher temperatures.

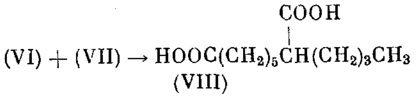
We have studied the reaction of cyclopentanone, cyclohexanone, cycloheptanone, and cyclododecanone with aqueous hydrogen peroxide over the temperature range 110-150°C. The effects of temperature, hydrogen peroxide concentration, and the molar proportions of the reagents on the composition and yields of the products have been examined in the case of cyclohexanone (Table 1). The results obtained show that the principal products are 1,10-decandicarboxylic (I), hexanoic (II), and adipic (III) acids, and caprolactone (IV). 1,10-Decanedicarboxylic acid is formed by a radical mechanism from α,α'-dihydroxydicyclohexyl peroxide (V), which is a product of the reaction of cyclohexanone with hydrogen peroxide. Thermal decomposition of (V) gives the alkoxyl radicals, which undergo β-decomposition to give 5-carboxy-pentyl radicals (VI), which apparently recombine in the solvent cell to yield 1,10-decanedicarboxylic acid (I):



(1)

In part, the radicals (VI) undergo rearrangement with 1,5-migration of hydrogen to form the α-carboxyalkyl radicals (VII). Subsequent recombination of radicals (VI) and (VII) gives 2-butylhexane-1,8-dicarboxylic acid (VIII). This reaction, however, is undergone by no more than 6-8% of the total reaction products of the 5-carboxypentyl radicals:

$$(VI) \rightarrow \underset{(VII)}{HOOC\dot{C}H(CH_2)_3CH_3} \qquad (2)$$



$$(VI) + (VII) \rightarrow \underset{(VIII)}{HOOC(CH_2)_5\overset{\overset{COOH}{|}}{C}H(CH_2)_3CH_3} \qquad (3)$$

The radicals (VI) diffuse to some extent from the solvent cell into the bulk of the solution, and react with cyclohexanone with hydrogen transfer to afford 2-oxocyclohexyl radicals (IX) and hexanoic acid. The radicals (IX) are converted into product molecules by mutual recombination or by combination with 5-carboxypentyl radicals (VI):

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