PREPARATION AND CERTAIN REACTIONS OF 3,3-DICYCLOPROPYLCYCLOPROPENE*

O. M. Nefedov, I. E. Dolgii,
E. V. Bulusheva, and A. Ya. Shteinshneider

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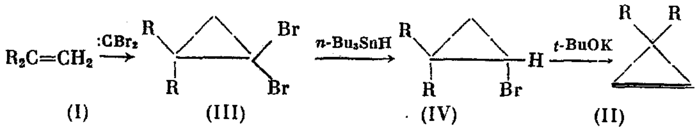
Among the polycyclopropanes and polycyclopropylcyclopropenes, the unsubstituted compounds are most unavailable. However, many of these compounds have unusual properties and can be used to most clearly observe the mutual interaction [interference] of the three-carbon rings.

The development of a simple method for the synthesis of a high-purity 1,1-dicyclopropylethylene (I) made it possible to prepare one of such compounds, 3,3-dicyclopropylcyclopropene (II)



R = cyclopropyl

The addition of dibromocarbene prepared from t-BuOK and $CHBr_3$ at ~−15°C to (I) in absolute pentane led to 1,1-dibromo-2,2-dicyclopropylcyclopropane (III) in a yield of 65%, whereas under similar conditions the yield of the corresponding dichloride from (I) and $CHCl_3$ is 50% [3]. During the formation of dibromocarbene by the action of 50% aqueous NaOH on $CHBr_3$ at ~40°C in the presence of triethylbenzylammonium bromide (TEBA) [4], compound (III) was obtained in a yield of 57%. According to GLC data, the product contained ~15% of an unsaturated compound with bromine attached to the multiple bond (the 1615 and 1590 cm^{-1} frequencies in the IR spectrum), indicating that under these conditions there is a partial opening of the dibromocyclopropane ring in (III).

The reduction of (III) by an equimolar amount of tributyl stannate at 40°C led to 1-bromo-2,2-dicyclopropylcyclopropane (IV) in a yield of 88%. Thus, no products of the complete reduction of dibromide (III) were observed. The dehydrobromination of the monobromide (IV) by the action of t-BuOK in DMSO at 20°C gave a 57% yield of (II). The structure of (II) was confirmed by elementary analysis, IR and PMR spectra. Thus, in the IR spectrum of (II), the 1630 cm^{-1} frequency corresponds to the C = C bond (compare 1629 cm^{-1} in 3,3-dimethylcyclopropene [5], 1640 cm^{-1} in 3,3-diphenylcyclopropene [6], and 1600 cm^{-1} in 3,3-dimethoxycyclopropene [7]). The singlet at δ 7.00 ppm in the PMR spectrum of (II) corresponds to the protons of the intracyclic double bond, which differs appreciably from the signals of the corresponding protons in 3,3-diphenylcyclopropene (6.12 ppm) [6], 3,3-dimethylcyclopropene (7.27 ppm) [5], and 3,3-dimethoxycyclopropene (7.77 ppm) [7], and is apparently due to the difference in the magnetic anisotropy of these substituents.

One of the characteristic chemical properties of 3,3-disubstituted cyclopropenes, due to the type of hybridization of the unsaturated carbon atoms in them, is the ability to readily undergo cyclodimerization into the corresponding tricyclo[3,1,0,$0^{2,4}$]hexanes. This was first observed in the photochemical irradiation of 1,3,3-trimethylcyclopropene in the presence of a sensitizer [8], and then in the case of other cyclopropenes in the presence of different catalysts [9, 10]. It was found that the cyclodimerization of (II) into 3,3,6,6-tetracyclopropyltricyclo[3,1,0,$0^{2,4}$]hexane (V), thermal or by the action of catalysts, proceeds much more readily than in the case of other 3,3-disubstituted cyclopropenes

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*For the previous article, see [1]. Part of this research was reported in a lecture at the 2nd All-Union Conference on Chemistry of Carbenes and Their Analogs [2].

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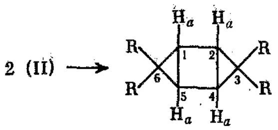

(V)

R = cyclohexyl.

In particular, during the distillation of (II) in vacuo, a residue forms in the flask, consisting mainly of (V). If (II) is heated for 2 h at 90°C, (V) is formed in a ~100% yield. A slow conversion of (II) into (V) is observed on prolonged holding of (II) at 0-5°C. The cyclodimerization of (II) by the action of BF_3 ethereate gives (V) in a lower yield (54%) because of strong resinification.

The structure of (V) was confirmed by elementary and spectral analysis. The PMR spectrum of (V) consists of a complex multiplet (of the AA'BB'C type) in the region from −0.2 to 1.4 ppm, induced by the protons of the cyclopropyl substitutents. Against this background, a singlet at 1.16 ppm is observed corresponding to the four angular protons. This shows that (V) has only one of two possible conformations of the tricyclohexane ring ("chair" or "boat"). Other signals (in particular, in the region of the double bond protons) were not observed in the spectrum. From the PMR spectrum of (V) only, it is difficult to attribute one or other conformation to the tricyclohexane ring. However, a simple analysis by means of Dreiding models shows that the boat conformation is extremely unfavorable even in the case of 3,3,6,6-tetramethyltricyclo[3,1,0,$0^{2,4}$]hexane, and especially for (V) with its more bulky cyclopropyl substituents. Thus, the chair conformation must be accepted for (V).

The tendency of the cyclopropene hydrocarbons to undergo thermal cyclodimerization was noted in [7] for 3,3-dimethoxycyclopropene, which forms inappreciable amounts of 3,3,6,6-tetramethoxytricyclo[3,1,0,$0^{2,4}$]hexane when left to stand for 6 h at 20°C. In contrast, according to [11], the thermal dimerization of 1-methylcyclopropene for 5 h at 20°C leads exclusively to 3-methyl-3-(2-methylcyclopropyl)cyclopropene, so that it was possible to suggest that in the absence of catalysts, the kinetically most favorable enic dimerization of cyclopropenes takes place preferentially. However, as in the thermodimerization of 3,3-dimethoxycyclopropene [7], in the case of thermal transformations of (II) under different conditions, we were unable to detect the products of enic dimerization.

We therefore studied the cyclodimerization of 3,3-dimethyl- and 1,3,3-trimethylcyclopropenes more thoroughly. After it was heated in a sealed tube for 25 h at 100-110°C, and for 8 h at 140°C, 3,3-dimethylcyclopropene remained practically unchanged. Under these conditions, and even under the action of BF_3 ethereate, 1,3,3-trimethylcyclopropene gave inappreciable amounts of high-molecular-weight products.

Thus, our data and literature data make it possible to conclude that 3-substituted cyclopropenes exhibit the greatest tendency to undergo cyclodimerization, and that this tendency increases with increase in the electronegativity of the substituents. Under these conditions 1,2-disubstituted cyclopropenes form preferably products of an enic dimerization or high-molecular-weight compounds.

EXPERIMENTAL

The GLC analysis was carried out on the LKhM-8MD apparatus with a katharometer; 300 × 0.2 cm columns with 5% SKTFT-50kh on chromosorb G, 80-10 μ; 15% Carbowax 20M on N-AW-DMCS and 15% Rheoplex-400 on N-AW-DMCS chromatone; carrier gas – helium, 30 ml/min.

The PMR spectra were run on the "Varian DA-60-IL" apparatus for solutions in CCl_4 with TMS as the internal standard. The ^{13}C NMR spectrum was run under pulse conditions with a broad band elimination of the proton noise, on the Bruker WP-60" apparatus with a working frequency of 60 MHz with reference to ^{13}C for a 30% solution in $CDCl_3$, with 5 vol. % of TMS as the internal standard. The IR spectra were recorded on the UR-20 spectrophotometer in a film of the substance on KBr.

1,3,3-Trimethylcyclopropene was prepared by the method given in [12].

1,1-Dibromo-2,2-dimethylcyclopropane (VI). A mixture of 30 ml of 50% aqueous NaOH, 20 g (~0.04 mole) of $CHBr_3$ and 0.2 ml of tributylamine was placed in a flask with a reflux condenser cooled to −40°C, and isobutylene was passed for 5 h at 20°C. The mixture was then diluted with water, washed with 2N H_2SO_4, and extracted with ether. From the extract, 10.2 g (56% based on $CHBr_3$) of (VI) were isolated bp 46-47°C (12 mm), n_D^{20} 1.5156, which corresponds to the data of [13].

1-Bromo-2,2-dimethylcyclopropane (VII). A 10.2 g (~0.02 mole) portion of n-Bu_3SnH was added in an N_2 atmosphere in the course of 1 h at 40°C to 8.1 g (~0.02 mole) of (VI). The mixture was stirred for 3 h. Distillation gave 2.4 g (~46%) of the bromide (VII), bp 104-105°C (760 mm), n_D^{20} 1.4516, which corresponds to the data of [14].

3,3-Dimethylcyclopropene (VIII). A solution of 0.17 mole of t-BuOK in 100 ml of DMSO was added in an N_2 atmosphere at 15°C to 12 g (0.08 mole) of (VII) in 15 ml of absolute DMSO. The mixture was stirred for 3 h, and after the addition of water, was slowly heated to 40°C. Thus, in a cooled (to −30°C) receiver 4.6 g (83%) of (VIII) were collected, bp 14-15°C. IR spectrum (ν, cm^{-1}): 1629 (C=C). PMR spectrum (δ, ppm): 1.13 ($2CH_3$), 7.27 s (2H in c-C_3H_2).

1,1-Dibromo-2,2-dicyclopropylcyclopropane (III). a) A 25.5 g (0.10 mole) portion of $CHBr_3$ was added dropwise in an N_2 atmosphere at −15°C to a mixture of 0.1 mole of t-BuOK in 50 ml of absolute pentane and 9 g (0.08 mole) of (I). The mixture was stirred for 3 h at −10°C, diluted at 20°C with water, and extracted with ether. From the extract, 15 g (65%) of (III), bp 112-113°C (6 mm); n_D^{20} 1.5500; d_4^{20} 1.6406 were isolated. Found: C 38.63; H 5.20; Br 56.48%. $C_9H_{12}Br_2$. Calculated: C 38.61; H 4.32; Br 57.07%. IR spectrum (ν, cm^{-1}): 685 (C−Br), 1020, 3010, and 3080 (cyclopropyl). PMR spectrum (δ, ppm): 0-0.8 m ($4CH_2$ in c-C_3H_5), 0.85-1.4 m (2CH in c-C_3H_5), 1.05 s (CH_2 in c-$C_3H_2Br_2$).

b) A 40 ml portion of 50% aqueous NaOH was added dropwise to a mixture of 16 g (0.14 mole) of (I), 38 g (0.15 mole) of $CHBr_3$, 0.5 ml of alcohol and 0.1 g of TEBA. The temperature rose to 40°C. The mixture was stirred for another 3 h at 40-45°C, and poured into 100 ml of water. From the organic layer, 14.5 g (57%) of (III) were isolated, bp 112-114°C (6 mm), containing, according to GLC, ~15% of an impurity with a somewhat longer retention time. IR spectrum (ν, cm^{-1}): 685 (C−Br), 1615 and 1590 (C=C).

1-Bromo-2,2-dicyclopropylcyclopropane (IV). A 15.4 g (0.05 mole) portion of n-Bu_3SnH was added in an N_2 atmosphere in the course of 1½ h at 40°C to 14.8 g (0.05 mole) of (III). The mixture was stirred for 4 h, and distilled. Yield 10 g (88%) of bromide (IV), bp 80-90°C (7-8 mm); n_D^{20} 1.5100; d_4^{20} 1.2985. Found: C 53.20; H 7.08; Br 39.86%. $C_9H_{13}Br$. Calculated: C 53.75; H 6.52; Br 39.73%. IR spectrum (ν, cm^{-1}): 680 (C−Br), 1025, 3010, and 3080 (cyclopropyl). PMR spectrum (δ, ppm): −0.2-0.8 m ($4CH_2$ in c-C_3H_5), 0.8-1.4 m (2CH in c-C_3H_5; CH_2 and CH in c-C_3H_3Br).

3,3-Dicyclopropylcyclopropane (II). A solution of ~0.28 mole of t-BuOK in 200 ml of DMSO was added dropwise in an N_2 atmosphere at 15°C to 25 g (0.12 mole) of (IV) in 100 ml of absolute DMSO. The mixture was stirred for 3 h, and after the addition of ice water, was extracted with pentane. Distillation of the extract yielded 8.6 g (57%) of cyclopropene (II), bp 75-77°C (65 mm), n_D^{20} 1.4770; d_4^{20} 0.8845. Found: C 89.87; H 9.90%. C_9H_{12}. Calculated: C 89.94; H 10.06%. IR spectrum (ν, cm^{-1}): 1630 (C=C), 1020, 3010, and 3080 (cyclopropyl). PMR spectrum (δ, ppm): −0.3 to 0.4 m ($4CH_2$ in c-C_3H_5), 0.9 to 1.4 m (2CH in c-C_3H_5), 7.0 s (2H in c-C_3H_5).

The residue in the distillation flask (1.5 g) was (V).

Thermal Cyclodimerization of (II). A 5-g portion of (II) was heated for 2 H at 90°C in a flask with reflux condenser. The mixture was cooled to 20°C, and 5 g (100%) of (V) mp 82-84°C, were obtained; after twice-repeated recrystallization from ethanol, mp 82-84°C. Found: C 89.85; H 10.16%. $C_{18}H_{24}$. Calculated: C 89.94; H 10.06%. PMR spectrum (δ, ppm); −0.2 to 0.8 m ($4CH_2$ in c-C_3H_5), 0.8 to 1.4 m (2CH in c-C_3H_5), 1.16 s (4CH in c-C_6H_4). ^{13}C NMR spectrum (in $CDCl_3$, δ, ppm): 42.23 (C^3, C^6), 24.48 (C^1, C^2, C^4, C^5), 11.45 (2α-C in equatorial c-C_3H_5), 10.72 (2α-C in axial c-C_3H_5), 1.98 (4β- and β'-C in equatorial c-C_3H_5), 0.82 (4β- and β'-C in axial c-C_3H_5).

Cyclodimerization of (II) under the Action of BF_3 Ethereate. A 3-g (~0.02 mole) portion of (II) was added in the course of 1 h to 0.5 ml of BF_3 ethereate in 5 ml of absolute ether. The temperature rose to 30°C, and the reaction mixture turned red-brown in color. The mixture was held for 1 h at 36-40°C, and 2 ml of 2N NaOH were added. The organic layer was separated, and dried over $CaCl_2$. After distillation of ether, 1.8 g of crystalline residue was obtained, from which (V) was isolated in a 54% yield, mp 85.5-86°C (from ethanol).

Cyclodimerization of 1,3,3-Trimethylcyclopropene under the Action of BF_3 Ethereate. A 1 ml portion of BF_3 ethereate in 3 ml of ether was added dropwise in the course of 40 min at 20°C to a solution of 5 g (0.07 mole) of 1,3,3-trimethylcyclopropene in 10 ml of absolute ether. The mixture was stirred for 1 h at 20°C and for 2 h at 35-40°C. It was then neutralized with 2N NaOH, and extracted with ether. The extract was dried and distilled. After distillation of ether and 1,3,3-trimethylcyclopropene, 3 g of undistillable polymeric residue and 0.8 g of a product boiling at 40°C (6 mm), and 105°C (3 mm) were obtained. IR spectrum (ν, cm^{-1}): 890 medium, 1160 weak, 1380 strong, 1640 medium, 1660 weak, 2730 weak, 2880 very pure, 2910-2970 very strong.

CONCLUSIONS

3,3-Dicyclopropylcyclopropene was synthesized and its high tendency to undergo quantitative thermal cyclodimerization into 3,3,6,6-tetracyclopropyltricyclo[3,1,0,$0^{2,4}$] hexane was shown.

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TELOMERIZATION OF ISOBUTYLENE WITH METHYL ESTERS OF PROPIONIC AND ISOBUTYRIC ACIDS

A. B. Terent'ev

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Telomerization of isobutylene with methyl chloroacetate is accompanied by the rearrangement of radicals with a 1,5-H-migration and cross-recombination of the telomeric radicals with isobutenyl radicals. Moreover, the dimer of the rearranged radical is formed in a high yield [1]. The present study is on the influence of the nature of the telogen on the course of the telomerization of isobutylene with carboxylic acid esters in the presence of tert-butyl peroxide.

For radical reactions with isobutylene, the allyl cleavage of the chain with the formation of isobutenyl radicals and their cross-recombination with growing radicals is characteristic. This path of the chain cleavage can play a very important role [1]. It is clear that telomerization of isobutylene with methyl isobutyrate proceeds without rearrangement and leads to the formation of two series of compounds, telomers (T_n) and products of cross-recombination of the growing radicals with the isobutenyl radicals (P_m)

$$\begin{gathered}(CH_3)_2CHCO_2CH_3 \xrightarrow{RO^\cdot} (CH_3)_2\dot{C}CO_2CH_3 \\ (CH_3)_2\dot{C}CO_2CH_3 + n(CH_3)_2C{=}CH_2 \rightarrow \underset{(A)}{{}^\cdot[(CH_3)_2CCH_2]_nC(CH_3)_2CO_2CH_3} \\ (A) + DH^* \rightarrow H[(CH_3)_2CCH_2]_nC(CH_3)_2CO_2CH_3(T_n) + D^\cdot \\ (A) + CH_2C(CH_3){=}CH_2 \rightarrow CH_2{=}C(CH_3)CH_2[(CH_3)_2CCH_2]_mC(CH_3)_2\cdot\ CO_2CH_3(P_m)\end{gathered} \qquad (1)$$

The yield of unsaturated compounds P_m is commensurable with the number of telomers T_n, and with the increase in the length of the radical chain, the relative yield of the unsaturated products increases by a factor of

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*Both the telogen and the monomer can play the role of a hydrogen donor (DH).

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