SOME THERMAL TRANSFORMATIONS OF 2-CYCLOPROPYL- AND 2,3-DICYCLOPROPYL-1,3-BUTADIENES

U. M. Dzhemilev, R. I. Khusnutdinov,
V. A. Dokichev, S. I. Lomakina,
L. M. Khalilov, G. A. Tolstikov,
and O. M. Nefedov

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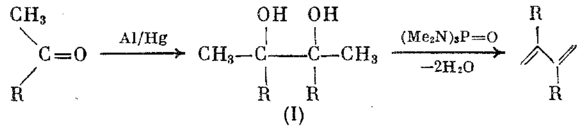
A few studies have been carried out on the thermal transformations of cyclopropyl-substituted 1,3-dienes. According to Frey [1] and Ketley [2], 1-cyclopropyl- and 1,1-dicyclopropyl-1,3-butadienes isomerize above 300°C to yield cyclopentene derivatives. There are no data on the thermal reactions of 2-cyclopropyl-1,3-butadiene (CPB) and 2,3-dicyclopropyl-1,3-butadiene (DCPB).

In this regard, we studied the cyclodimerization under Diels–Alder reaction conditions and high-temperature conversions of CPB [3] and of DCPB (not reported previously). DCPB was synthesized in high yield in 58% yield by the dehydration of 2,3-dicyclopropyl-2,3-butanediol (I) obtained in 30% yield by the condensation of methyl cyclopropyl ketone in the presence of aluminum amalgam



R = cyclopropyl.

At 160-200°C, CPB forms a mixture of three cyclodimers (II), (III), and (IV) in yields up to 70% and a mixture of higher-molecular-weight oligomers in 20-30% yields (Table 1). The reaction selectivity increases somewhat using benzene or toluene solvents. The ratio of the cyclodimers formed from CPB changes only slightly from run to run and averages 28% (II), 26% (III), and 46% (IV).

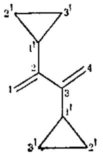
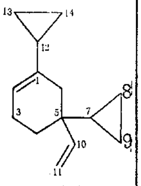
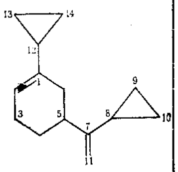
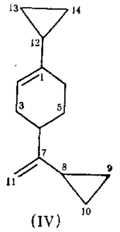
The individual compounds (II), (III), and (IV) were separated by preparative gas–liquid chromatography and their properties are given in Table 2.

TABLE 1. Effect of Reaction Conditions on the Yield of Cyclic Dimers of 2-Cyclopropyl-1,3-butadiene, (II)-(IV)

T, °C	Time, h	Solvent	Conversion of CPB, %	Dimer yield, %	Oligomer yield, %
160	5	–	60	38,2	21,8
160	8	–	75	50	25
180	5	–	73,7	46,7	27
180	8	–	93	64,5	28,5
200	5	–	95	68	27
200	8	–	100	70,7	29,3
180	8	Benzene	82	66,7	15,3
180	8	Toluene	79,5	67	12,5
200	8	Benzene	89	72,5	16,5
200	8	Toluene	87	73	14
200	10	»	93	71	22
200	12	»	97	68	29

Institute of Chemistry, Bashkir Branch of the Academy of Sciences of the USSR, Ufa. N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2071-2077, September, 1981. Original article submitted December 8, 1980.

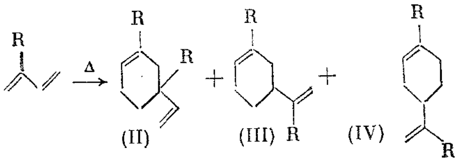
TABLE 2. Characteristics of Compounds Obtained

Compound	bp, °C (p, mm Hg)	n^{20}_D	IR-spectra ν, cm^{-1}	PMR spectra, δ, ppm	^{13}C NMR spectra, δ, ppm	Mass spectra, M+
(I)	74–75(1)	1,4854	1028, 3090 (CPR) 3400–3500 (OH)	0,25–0,32 (8H, CH_2 in CPR) 0,8–1,6 (2H, CH in CPR) 1,07 (6H, CH_3), 2,2 (2H, OH)	–	170
	75(30)	1,4910	840, 900, 1600, 3090, (diene system), 1030, 3100 (CPR)	0,31–0,72 (8H, CH_2 in CPR) 1,08–1,90 (2H, CH in CPR) 4,75–5,21 (4H, olefinic protons)	4,92 ($C^{2'}$, $C^{3'}$), 13,72 ($C^{1'}$), 108,35 (C^1, C^4), 147,50 (C^2, C^3)	134
 (II)	85(2)	1,5109	840 (trisubstituted double bond) 920, 980, 3090 (vinyl group) 1022, 3090 (CPR)	0,1–0,7 (9H, CH_2 and CH in CPR), 1,1-1.90 (1H, CH in CPR), 1.40-1.48 (2H, CH in cyclohexene), 1.90 (4H allylic protons), 4.90, 5.20-5.56 (4H olefinic protons)	136,9 (C^1), 117,3 (C^2), 24,51 (C^3), 31,69 (C^4), 37,0 (C^5), 34,15 (C^6), 19,71 (C^7), –, 0,62 (C^8), 0,16 (C^9), 141,1 (C^{10}), 112,5 (C^{11}), 17,06 (C^{12}), 4,44 (C^{13}), 4,24 (C^{14})	188
 (III)	87–88(2)	1,5141	830 (trisubstituted double bond) 890, 1642, 3085 (C=CH_2), 1028, 3085 (CPR)	0,2–0,58 (8H, CH_2 in CPR), 1,20–1,6 (4H, CH in CPR and CH_2 in cyclohexene, 1,94 (4H allylic protons), 4,50, 5.28 (3H olefinic protons)	137,4 (C^1), 118,7 (C^2), 25,74 (C^3), 28,40 (C^4), 41,09 (C^5), 33,32 (C^6), 154,7 (C^7), 14,86 (C^8), 6,64 (C^9, C^{10}), 104,2 (C^{11}), 17,39 (C^{12}), 4,83 (C^{13}), 4,12 (C^{14})	188
 (IV)	91–92(2)	1,5157	840 trisubstituted double bond) 890, 3075 (C=CH_2), 1028, 3090 (CPR)	0,2–0,65 (8H, CH_2 in CPR), 1.18-1.6 (4H, CH in CPR and CH in cyclohexene), 1.84-2.0 (4H allylic protons), 4.5, 5.30, (3H olefinic protons)	137,0 (C^1), 118,8 (C^2), 27,55 (C^3), 41,35 (C^4), 31,57 (C^5), 28,57 (C^6), 154,6 (C^7), 14,86 (C^8), 6,45 (C^9), 6,58 (C^{10}), 104,0 (C^{11}), 17,19 (C^{12}), 4,76 (C^{13}), 4,05 (C^{14})	188
(V)	132(0,5)	1,5301	895, 3080 (C=CH_2), 1030, 1040, 3090 (CPR)	0,2–0,66 (16H, CH_2 in CPR), 0,86–1,6 (3H, CH in CPR), 1.2-1.3 (3H, CH in CPR and CH_2 in cyclohexene), 2.18 (4H, allylic protons), 4.43 (2H, =CH_3)	–	268
(VII)	70(8)	1,5217	930 trisubstituted double bond), 890, 3070 (C=CH_2), 1030, 3090 (CPR)	0,33–0,69 (4H, CH_2 in CPR), 1,2–1,8 (1H, CH in CPR), 1,92 (2H, CH_2 in cyclopentene), 2.47 (4H, allylic protons), 4.80 (2H, =CH_2), 6.09 (1H, CH)	–	134

The molecular weight of (II), (III), and (IV) was found to be 188 using mass spectroscopy. The IR spectrum of (II) has bands at 840, 920, 980, 1640, 1029, and 3090 cm^{-1}, which are characteristic for a trisubstituted double bond, vinyl group, and cyclopropane ring (CPR). The PMR spectrum of (II) displays a signal at 4.9 ppm which corresponds to terminal vinyl protons and a complex multiplet at 5.2-5.6 ppm arising due to olefinic protons. The presence of cyclopropyl groups in (II) is indicated by the multiplet at 0.1-0.7 ppm. The IR spectra of (III) and (IV) are characterized by the presence of bands at 840, 890, 1028, 3030, and 3090 cm^{-1}, which were assigned to a trisubstituted double bond, methylene group, and CPR. The PMR spectra of (III) and (IV) are virtually identical.

A more rigorous determination of the structures of (II), (III), and (IV) was carried out by analyzing their ^{13}C NMR spectra (δ, ppm). The upfield signals in the spectrum of (II) at 4.44 m and 4.24 m ($J_{CH}=160.1$), −0.62 m ($J_{CH}=158.2$), 17.06 d ($J_{CH}=155.3$), and 19.71 d ($J_{CH}=160$) indicate the presence of two CPR in (II) [4]. The doublet at 117.3 and singlet at 136.9 were assigned to C^1 and C^2 of the cyclohexene ring. Rather similar signals were obtained in the ^{13}C NMR spectra of (III) and (IV) (see Table 2) which differ from the spectrum of (II) mainly in the position of the vinyl group carbon atoms. In particular, the vinyl group in (II) has a multiplet at 112.5 ppm and a doublet at 141.7 ppm, while the terminal methylene groups in (III) and (IV) give a multiplet at 104.2 ppm and singlet at 154.7 ppm which are characteristic for 1,1-disubstituted double bonds.

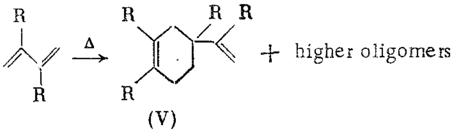
Exhaustive information on the structures of (II), (III), and (IV) was obtained after comparing their spectra with the ^{13}C NMR spectra of model 1-methyl-4-phenyl- and 1-methyl-5-phenyl-1-cyclohexenes [5]. The spectra of (II) and (III) have a set of signals characteristic for 1,5-disubstituted 1-cyclohexene [24.51, 31.69, 34.15, 37.0, 117.3, and 136.9 ppm for (II) and 25.74, 28.40, 33.32, 41.09, 118.7, and 137.4 ppm for (III)], while the spectrum of (IV) corresponds to a 1,4-disubstituted 1-cyclohexene (27.55, 28.57, 31.57, 41.35, 118.8, and 137.1 ppm) [5].



R = cyclopropyl.

These spectral data for CPB cyclodimers permitted assignment of structures 1,5-dicyclopropyl-5-vinyl-1-cyclohexene (II), 1-cyclopropyl-5-(1-cyclopropylvinyl)-1-cyclohexene (III), and 1-cyclopropyl-4-(1-cyclopropylvinyl)-1-cyclohexene (IV).

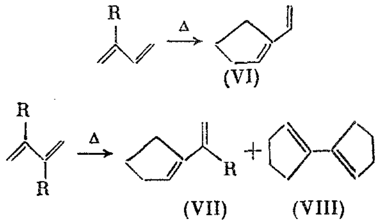
Heating DCPB at 200°C for 17 h leads to a mixture of hydrocarbons containing ~ 38% dimer (V) with a six-membered ring and ~ 47% higher oligomers whose identification is extremely difficult. The conversion of DCPB in these experiments is ~ 85%. Attempts to increase the selectivity relative to (V) by changing the dimerization condensation were unsuccessful. The structure of (V) was established using IR, NMR, and mass spectrometry.



R = cyclopropyl.

In analogy to the previously described isomerization of cyclopropyl derivatives of 1,3-dienes above 300°C to yield cyclopentene derivatives [1, 2], we studied the reactions of CPB and DCPB at 250-500°C. Thermal isomerization of CPB is observed at 350°C and yields the known 1-vinyl-1-cyclopentene (VI) [6] and high-molecular-weight hydrocarbons whose yield increases with increasing temperature, reaching a maximum of ~ 72% at 500°C (Table 3).

In contrast to CPB, the thermal isomerization of DCPB occurs in a more complex manner, accompanied by the formation of the products of both partial and complete isomerization of DCPB (Table 4) and leading to the formation of 1-(1-cyclopropylvinyl)-1-cyclopentene (VII) and 1,1-bicyclopentenyl (VIII). Unfortunately, we were unable to increase the selectivity of this reaction, though carrying out the reaction in aromatic solvents significantly diminishes the yield of high-molecular-weight oligomers. Table 4 shows that the total yields of (VII) and (VIII) increase with increasing isomerization temperature, but the reaction selectivity drops significantly. The structure of (VII) was proven by spectral methods, while the structure of (VIII) was demonstrated by comparison to a known sample [7].



R = cyclopropyl.

TABLE 3. Effect of Temperature on the Isomerization of 2-Cyclopropyl-1,3-butadiene

Reaction temp, °C	CPB conversion, %	Yield of 1-vinyl-1-cyclopentene, % *
250	0	0
300	3	0
350	8	89
400	19	81
450	37	79
500	95	72

*Relative to reacted monomer.

TABLE 4. Temperature Dependence of the Yield and Composition of the Products of the Isomerization of 2,3-Dicyclopropyl-1,3-butadiene

Reaction temp, °C	DCPB conversion, %	Yield, % *	
		(VII)	(VIII)
250	0	0	0
300	5	0	0
350	8	93	0
400	17	70	12
450	43	65	14,8
500	66	40	36

*Relative to reacted DCPB.

Thus, we are the first to report the cyclodimerization of CPB, DCPB and previously undescribed derivatives of cyclohexene with the retention of the cyclopropyl ring as well as the high-temperature isomerization of CPB and DCPB, which occurs with opening of the cyclopropyl ring and formation of cyclopentene derivatives.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were taken on Tesla BS-480 and Bruker WH-90 spectrometers for CCl_4 solutions with TMS internal standard. The IR spectra were recorded on a UR-20 spectrometer, and the UV spectrum was taken on a Specord UV-VIS spectrometer for ethanolic solutions. The mass spectra were taken on an MKh-1306 spectrometer. The gas–liquid chromatographic analysis was carried out on a Tsvet-102 chromatograph using a 1-m-long column packed with 5% SE-30 on Chromaton N-AW; helium was the carrier gas. The preparative separation was carried out on a Khrom-31 chromatograph using a 1.5-m-long column packed with 20% E-301 on Chromaton N-AW.

A sample of 2-cyclopropyl-1,3-butadiene (CPB) was obtained by the method of Golovchanskaya [3] and subjected to triple distillation to give 99% purity.

2,3-Dicyclopropyl-2,3-butanediol (I). To 21 g (0.78 g-atom) aluminum filings in 150 ml dry benzene at reflex, a solution of 10.8 g (0.04 mole) $HgCl_2$ in 105 g (1.25 mole) methyl cyclopropyl ketone was added dropwise. The mixture was heated at reflux for 2 h, cooled, and 120 ml benzene and 90 ml water were added and this mixture was heated for 1 h at 100°C. The precipitate was filtered off and washed with three 150-ml portions of benzene. The solution obtained was dried over Na_2SO_4, and the benzene was distilled off. The residue was distilled in vacuum to yield 31.5 g (30%) (I).

2,3-Dicyclopropyl-1,3-butadiene (DCPB). A mixture of 22 g (0.13 mole) diol (I) and 127.2 g (0.78 mole) HMPTA was heated for 1 h at 215-240°C. The flask contents were cooled, diluted with water, and extracted with five 50-ml portions of pentane. The extract was washed twice with 50 ml water, dried over Na_2SO_4, the pentane was evaporated, and the residue distilled in vacuum to yield 10 g (58%) DCPB. UV spectrum: λ_{max} 229.3 nm (ε 19,100) (in ethanol).

Dimerization of 2-Cyclopropyl-1,3-butadiene. A mixture of 9.4 g (0.1 mole) CPB, 0.1 g stabilizer, and 20 ml toluene was heated in a steel autoclave for 8 h at 200°C. Distillation yielded 1.2 g CPB, 6.9 g (73%) mixture of cyclodimers (II), (III), and (IV), and 1.3 g (14%) undistilled residue.

Dimerization of 2,3-Dicyclopropyl-1,3-butadiene. A mixture of 4.1 g (0.03 mole) DCPB, stabilized with bisphenol, and 4 ml benzene was heated in a 15-ml steel bomb at 200°C for 17 h. The conversion of DCPB was 85%. Distillation yielded 1.55 g (37.8%) (V) and 1.93 g (47.2%) higher oligomers.

Thermal Isomerization of CPB and DCPB. Experiments on the thermal isomerization were carried out by introducing a 30% solution of CPB or DCPB in benzene through a 350 × 10-mm quartz tube filled with 5 × 3-mm quartz rings at 0.5-1.0 ml/min. The use of an inert diluent decreases tar formation by 10-30%. An SUOL-0.25 unit was used for heating. The physical constants for the compounds obtained are given in Table 2.

CONCLUSIONS

1. 2,3-Dicyclopropyl-1,3-butadiene was synthesized.

2. The feasibility was shown for the production of cyclopropyl derivatives of cyclohexene by the thermal cyclodimerization of 2-cyclopropyl- and 2,3-dicyclopropyl-1,3-butadienes at 160-200°C.

3. The isomerization of 2,3-dicyclopropyl- and 2-cyclopropyl-1,3-butadienes above 350°C is accomanied by opening of the cyclopropane ring and formation of cyclopentene derivatives.

LITERATURE CITED

1. H. M. Frey and A. Krantz, J. Chem. Soc., A, 1159 (1969).
2. A. D. Ketley, J. L. McClanahan, and L. P. Fisher, J. Org. Chem., 30, 1659 (1965).
3. A. P. Golovchanskaya, Zh. Obshch. Khim., 11, 608 (1941).
4. G. Levy and G. Nelson, Carbon-13 Nuclear Magnetic Resonance Handbook for Organic Chemists [Russian translation], Izd. Mir, Moscow (1975), p. 68.
5. K. Nakagawa, M. Sawai, Y. Ishii, and M. Ogawa, Bull. Chem. Soc. Jpn., 50, 2487 (1977).
6. S. F. Birch, R. A. Dean, N. J. Hunter, and E. Whitehead, J. Org. Chem., 20, 1178 (1955).
7. R. Ya. Levina, V. R. Skvarchenko, and O. Yu. Okhlobystin, Zh. Obshch. Khim., 25, 1466 (1955).

OXIDATIVE ADDITION OF 1,3-DICARBONYL COMPOUNDS TO DIENES IN THE PRESENCE OF Mn(III) AND Cu(II) ACETATES

M. G. Vinogradov, M. S. Pogosyan,
A. Ya. Shteinshneider and G. I. Nikishin

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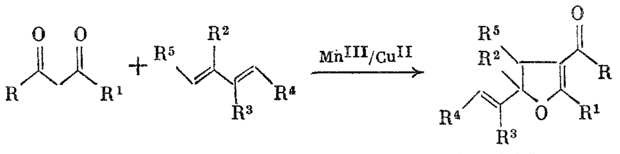
The use of the compounds of transition metals in the chemistry of 1,3-dienes is mostly concerned with catalytic oligomerization processes [1]. Catalytic reactions of other types and addition of functionality substituted organic compounds to 1,3-dienes, in particular, have been studied little [2-7]. They relate mainly to the production of unsaturated halogen derivatives and amines from polyhalogenoalkanes, hydroxylamines, and N-chloroamines in the presence of copper(II), iron(II), ruthenium(II), and titanium(III) salts.

We realized the oxidative 1,2-addition of acetyl acetone (AA) and other 1,3-dicarbonyl compounds to conjugated dienes in the presence of manganese(III) acetate and catalytic amounts of copper(II) acetate.* 5-(1-Alkenyl)-4,5-dihydrofurans (I-XII) are formed selectively as a result of this reaction (Table 1).



(I)—(XII)

Acetate has a significant effect on the selectivity of the process. For instance, 2-methyl-3-acetyl-5-vinyl-4,5-dihydrofuran (I) is not formed at all from AA and butadiene in the absence of copper acetate. The yield of the dihydrofuran (I) increases with increase in the concentration of copper (II) and reaches a maximum at $[Cu(II)] = 3\text{-}5 \cdot 10^{-2}$ M. Further increase in the concentration of copper(II) does not have a significant effect on the reaction path. If butadiene is bubbled through an acetic acid solution containing AA (0.15 M), manganese(III) acetate (0.1 M), and copper(II) acetate ($5 \cdot 10^{-3}$ M) at ~ 20°C for 6 h or a mixture of the reagents is heated at 60°C for 15 min, the dihydrofuran (I) is obtained with a yield of 97%.

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* Earlier we reported on the oxidative addition of AA and acetoacetic ester to ethylene [8], 1-alkenes, and styrene [9].

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