FORMATION OF THE PRODUCTS OF [1 + 2]- AND [2 + 2]-CYCLOADDITION IN THE CATALYTIC REACTION OF CYCLOPROPENES WITH UNSATURATED POLYCYCLIC HYDROCARBONS\*

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We previously showed that the catalytic reaction of cyclopropene hydrocarbons with olefins yields vinylcyclopropanes, formed as a result of isomerization of cyclopropenes [2] or bicyclo [2.1.0] pentanes, the products of intermolecular cross-[2 + 2]-cycloaddition [3]. The direction of the reaction is essentially dependent on the character of the double bonds of the olefin and particularly on the ligand environment of the CuCl used as the catalyst [3]. For example, hydrocarbons of the norbornene type which contain a strained double bond can react with cyclopropenes in both directions indicated at the same time [1, 4], and the reaction takes place with a high selectivity according to the type of [2 + 2]-cycloaddition in the presence of (PhO)<sub>3</sub>P·CuCl at -20°C and especially Ph<sub>3</sub>P·CuCl at 20°C [3].

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In developing these studies, the reactions of 3,3-dimethyl-(Ia), 3-methyl-3-cyclopropyl-(Ib), and 1,3,3-trimethylcyclopropenes (Ic) with unsaturated hydrocarbons containing a bicyclo[2.2.1]heptene fragment, catalyzed by CuCl or a complex of CuCl with  $(PhO)_3P$ : norbornadiene (NBD), 5-methyl-2-norbornene (MNB), endo- and exo-dicyclopentadienes (DCPD), exo, endo-tetracyclo[6.2.1.1.<sup>3,6</sup>.0<sup>2,7</sup>]-4-dodecene (TCD), and exo-trans, exo-pentacyclo-[8.2.1.14,702,9.03,8]-5,11-tetradecadiene (PCT), were investigated in the present study. The experiments were conducted in the range from -20 to 40°C by adding 1-3 mole % catalyst mixture of cyclopropene, olefin, and  $CH_2Cl_2$  in the molar ratio of 1:4-6:4-8. to a In these conditions, adducts of cross-cycloaddition of cyclopropenes to the double bonds of the unsaturated hydrocarbons are formed together with the products of homodimerization of the cyclopropenes, and the ratio of adducts of [2 + 2]-cycloaddition and the corresponding isomeric products of vinylcyclopropanation is essentially a function of the conditions of the reaction and the nature of the starting reactants. The reaction of cyclopropene (Ia) with NBD in the presence of (PhO)<sub>3</sub>P·CuCl at -20°C results in a [2 + 2]-cycloadduct: 4,4-dimethylexo, trans-tetracyclo[5.2.1.0<sup>2</sup>, <sup>6</sup>.0<sup>3,5</sup>]-8-decene (IIa) with a yield of 60%. However, at 40°C, the product of vinylcyclopropanation is basically formed: anti-3-(2-methylpropen-1-yl)-exoand endo-tricyclo[3.2.1.0<sup>2,4</sup>]-6-octene(IIIa), whose yield is 68% with a yield of (IIa) of a total of 7% (Table 1).



$$\begin{split} R = H, \quad R^1 = Me \ (a), \ cyclo-C_3H_5 \ (b); \quad R = R^1 = Me \ (c); \\ Cat = CuCl \quad \text{or} \ (PhO)_3P \cdot CuCl. \end{split}$$

The reaction of NBD with cyclopropene (Ib) takes place analogously, and as previously observed [3], virtually 4-methyl-4-cyclopropyl-exo,trans-tetracyclo[5.2.1.0<sup>2</sup>,<sup>6</sup>0<sup>3</sup>,<sup>5</sup>]-8-decene (IIb) alone is formed at -20°C in the presence of  $(PhO)_3P$ ·CuCl. However, increasing the temperature of the reaction to 40°C results in the formation of the product of [1+2]-cyclo-addition: 3-(2-cyclopropylpropen-1-yl)-exo- and endo-tricyco[3.2.1.0<sup>2</sup>,<sup>4</sup>]-6-octene (IIIb), whose yield attains 40%, in addition to (IIb). The use of CuCl as the catalyst causes even

# \*For previous communication, see [1].

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|                               |   |   |                                     | Yield, %   |                        |                            |
|-------------------------------|---|---|-------------------------------------|--|------------------------|----------------------------|
| Starting<br>cyclo-<br>propene | Catalyst, 1.5 mole%                                   | Т,°С  | exo-(II)                            | (III)<br>(exo:endo)  | (IV)                   | (V)                        |
| (Ia)                          | (PhO)₃P·CuCl<br>»                                     | -20 40  | 60<br>7                             | 10 (3,7 : 1)<br>68 (3,5 : 1)   | 12<br>6                | 10                         |
| (Ib)                          | (PhO) <sub>3</sub> P·CuCl<br>*<br>CuCl<br>*<br>Absent | $ \begin{array}{r} -20 \\ 20 \\ 40 \\ -20 \\ 20 * \\ 150 * \\ \end{array} $ | 94<br>72<br>42<br>10<br>16<br>55-60 | $\begin{array}{c} - \\ 15 & (4:1) \\ 40 & (3,9:1) \\ 27 & (4:1) \\ 75 & (4:1) \\ 27 & (3,9:1) \end{array}$ | 5<br>3<br>4<br>-<br>13 | $-\frac{8}{12}$<br>56<br>7 |
| (Ic)                          | (PhO) ₃P·CuCl   | 20  | -                                   | 55 (5:1)   | _                      | 30                         |

TABLE 1. Composition of the Products of the Reaction of Norbornadiene with 3,3-Dimethyl- (Ia), 3-Methyl-3-cyclopropyl (Ib), and 1,3,3-Trimethylcyclopropene (Ic) ( $\sim$ 6:1 molar ratio of reactants)

\*∿10:1 ratio of reactants.

greater formation of (IIIb) (Table 1). Despite an excess of NBD, partial dimerization of the cyclopropenes takes place in almost all cases, both with preservation of the three-carbon rings (formation of tricyclo[ $3.1.0.0^2$ , <sup>4</sup>]hexanes (IV)), and their isomerization [formation of the corresponding hexatrienes (V)].

In the reaction of NBD with 1,3,3-trimethylcyclopropene (Ic) in the presence of  $(PhO_3)_3P$ . CuCl at 20°C, 3-(1,2-dimethylpropen-1-yl)-exo- and endo-tricyclo[3.2.1.0<sup>2</sup>,<sup>4</sup>]-6-octene (IIIc) and the previously described [5] 2,3,6,7-tetramethyl-2,4,6-octatriene (Vc) were identified as the basic products, and the yields were 55 and 30%, respectively.

As Table 1 shows, the use of noncomplexed CuCl or an increase in the temperature sharply increases the yield of vinylcyclopropane adducts (III) in comparison to [2 + 2]-cycloadducts (II). This increase in the yields of (III) is probably due to potentiation of the effect of the copper ion on the cyclopropene ring, which causes opening of the strained ring to a greater degree and the occurence of a reaction along the [1 + 2]-cycloaddition pathway as energetically more advantageous in comparison to [2 + 2]-cycloaddition. It is interesting to note that the thermal reaction of (Ib) with an excess of NBD also results in the corresponding products of cross-cycloaddition (IIb) and (IIIb) [1], and the isomeric composition of the products of vinylcyclopropanation of (IIIb) is almost identical to the corresponding adducts of catalytic cycloaddition.

The structure and isomeric composition of vinyltricyclooctenes (III), isolated from the reaction mixture by preparative TLC or column chromatography (silica gel, eluent: hexane) were established based on the high-resolution PMR spectra. It was found that unsaturated hydrocarbons (IIIa, c) are mixtures of two isomers in the ratio of (3.5-5):1, and (IIIb) is a mixture of four isomers caused by the E,Z-isomerism of the 2-cyclopropylpropenyl fragment, whose spectral characteristics were examined in [2]. The choice between exo-, endo-, syn-, and anti-isomers of (III) was made in consideration of the chemical shifts of the olefin protons and the multiplet character of the signals of the H<sup>b</sup> cyclopropane proton. The significant difference in the chemical shifts of the signals of the olefin protons of the norbornene fragment in the region of  $\delta$  6.34-6.37 and 5.78-5.80 ppm for all isolated (III) indicates the presence of an exo- and endo-tricyclooctene fragment, since this difference is characteristic of the signals of protons of unsubstituted exo- and endotricyclo[3.2.1.0<sup>2</sup>,<sup>4</sup>]-6-octenes, which respectively appear in the region of  $\delta$  6.35 [6] and 5.65 ppm [7].

The anti orientation of the vinyl group in the predominantly formed exo isomers (III) clearly follows from the multiplet character of the signal of the H<sup>b</sup> methine proton, since the observed value of the SSCC  $J_{bc} = 2.6-2.8$  Hz is characteristic of the trans protons of the cyclopropane ring. It was difficult to make a similar assignment for the minor isomers of (III) due to the overlapping of the corresponding signals by other groups of protons. For this reason these isomers were identified on the example of isomeric dienes (IIIb) by monocyclopropanation into adducts (VIb) due to the effect of a small excess of diazomethane in

TABLE 2. Properties of Adducts of [1 + 2]-Cycloaddition of Cyclopropenes (Ia + c) to Polycyclenes

| -       | BP, °C                                      |           | Isomeric                        | com-                | PMR spectru                   | m (CDCl <sub>3</sub> ; δ,  | ppm; J Hz)                  | -       |                                 |                 |  |
|---------|---|-----------|---------------------------------|---------------------|-------------------------------|--|-----------------------------|---------|---------------------------------|-----------------|--|
| punod   | (mm)(p,<br>mm Hg)                           | ILC, KF   | isomer                          | concen-<br>tration, | Ч                             | P.H.   | Hc, Hc                      | "ри     | CH,                             | HC=CH           | other protons  |
| (IIIa)  | 8486<br>(18)                                | 0,31-0,37 | exo                             | 75-78               | 4.62<br>d.sp                  | 2.53<br>d.t  | 0,91<br>br.d.               |         | 1,75d,<br>1,66 d                | 6,35 t<br>1~2,1 | 2.85 m (H <sup>1</sup> , H <sup>5</sup> ), 1.23 m<br>(H <sup>9</sup> -anti), 0.91 m (H <sup>9</sup> -syn,  |
|         |   |           | endo                            | 22-25               | Jab = 9.1<br>4.68<br>d.sept   | $J_{bc} = 2.7$<br>1.3**  | 1,3 ***                     |         | /~1,5<br>1,65 d,<br>/~1,5       | 5,80 t<br>J~2,1 | $\begin{array}{l} J_{\text{gem}} \sim 8.9 \\ 2.87 \text{ m} (\text{H}^{1}, \text{H}^{5}), 1.75\% \text{ and} \\ 1.3\%(2 \text{H}^{3}) \end{array}$ |
| (q111)  | 78-81<br>(1)                                | 0,27-0,35 | exo, E                          | 50-52               | Jab = 9.0<br>4.72<br>d.qu     | 2.57<br>d.t  | 0,97<br>br.d                | 1,32 †  | 1,62 d<br>J=1,5                 | 6,37 ш          | 2.85 m (H <sup>1</sup> , H <sup>5</sup> ), 1.25 <sup>%%</sup><br>(H <sup>8</sup> -anti), 0.89 br.d   |
|         |   |           | exo, Z                          | 29-31               | Jab = 8.6<br>4.75 m           | $\frac{J_{bc}}{2.80} = \frac{2.6}{d.t}$  | 0,98<br>br.d                | 1,85 m  | 1,38 d                          | 6,37 m          | (H <sup>8</sup> -syn, J <sub>gem</sub> ~ 9.5)<br>0.70-0.37 (CH <sub>2</sub> in cyclo-  |
|         |   |           | endo, E                         | 10-12               | $J_{ab} = 8.5$ 4.79 d.ou      | J <sub>bc</sub> = 2.6  | /bc=2,6                     | 1,3 +   | √=1,5<br>1,54 d<br>1~1,5        | 5,80 m          | <sup>U3H5)</sup><br>2.86 m (H <sup>1</sup> , H <sup>5</sup> ), 1.65 <sup>%%</sup><br>(H <sup>2</sup> -syn), 1.28 <sup>%%</sup>                     |
|         |   |           | endo, Z                         | 6-8                 | $\int_{ab}^{ab} = 9.4$ 4.82 m | **   | yest                        | 1,78†   | 1,36 d<br><i>J</i> ~1,5         | 5,80 m          | (H <sup>2</sup> -anti); 0.70-0.37<br>(CH <sub>2</sub> in cyclo-C <sub>3</sub> H <sub>5</sub> )   |
| (111c)  | 8083<br>(9)                                 | 0,28-0,34 | exo                             | 65-68               | Jab ~ 9.4                     | 2.61   | 1,05  br. d<br>1,=2,9<br>bc |         | 1,78 9,<br>1,63 br.s<br>1,45 qu | 6,35 t<br>J=1,9 | 2.83 m (H <sup>1</sup> , H <sup>5</sup> ), 1.26 (H <sup>8</sup> -<br>anti), 0.85 br.d(H <sup>8</sup> -syn,<br><sup>J</sup> gem = 9.2)              |
|         |   |           | endo                            | 32-35               |                               | ***  | şçəş                        |         | /~1,0<br>1,68,                  | 5,78<br>J=2,1   | 2.87 m (H <sup>1</sup> , H <sup>5</sup> ), 1.7 <sup>***</sup> (H <sup>8</sup> -<br>syn), 1.32 (H <sup>8</sup> -anti)                               |
| (q1)    | 9296<br>(1)                                 |           | ехо, Е                          | 50-52               | 4.63 d.qu<br>Jab_= 8.8        | 1.86 d.t<br>J <sub>bc</sub> = 2.6  | 0,98 **                     | 1,3 *** | 1,45<br>1,60 d<br>1,1,4         |                 | 0.97 (H <sup>9</sup> ), 0.72 d.t (H <sup>7</sup> -syn,<br>Jgem = 5.4. Jtrans = 3.4)  |
|         |   |           | exo, Z                          | 28-31               | $J_{ab} \sim 9.0$             | $\begin{bmatrix} 2.08 & d.t \\ Jab = 9.0 \\ I \end{bmatrix}$   | 0,98 ***                    | 1,791   | 1,40 d<br>J=1,4                 |                 | 0.65-0.35 (CH <sub>2</sub> in cyclo-<br>C <sub>3</sub> H <sub>5</sub> ), 0.21 d.t. (H <sup>7</sup> -anti.  |
| _       |   |           | endo, E                         | 10-13               | 4,65**                        | $\frac{3}{2}$ $\frac{3}{62}$ $\frac{2}{62}$ $\frac{1}{6}$ $\frac{1}{6}$ $\frac{1}{2}$ $$ | **                          | 1,25 b  | 1,65 đ<br>J~1,5                 |                 | $J_{gem} = 5.4$ , $J_{cis} = 7.4$ )<br>1.25 <sup>348</sup> (H <sup>6</sup> , H <sup>8</sup> ), 1.58 and<br>0.89 m (2H <sup>9</sup> ), 0.65-0.35    |
|         |   |           | endo, 2                         | 6-9                 | 4.68 m                        | $\frac{1}{2}$ bc = 2./<br>2.85 d.t<br>Jab = 9.2  | **                          | 1,78†   | 1,41 d<br>1~1,4                 |                 | $(H^7 - syn and CH_2 in cyclo-C3H5), 0.02 d.t. (H7-anti,$  |
| (q1117) | $\begin{array}{c} 90-95 \\ (1) \end{array}$ | 0,40-0,46 | E, (endo-<br>(CH <sub>3</sub> ) | 50-52               | 4.59 d.qu<br>$J_{ab} = 8.9$   | $\frac{J_{bc}}{1.53} = 2.7$  | 0,7 mts                     | 1,32†   | 1,61 d                          |                 | $J_{\text{gem}} = 5.2, J_{\text{cis}} \sim 8.0$ )<br>2.29 and 2.15 m (H <sup>2</sup> , H <sup>5</sup> ) 1 g  |
|         |   | . <u></u> | Z, (endo-<br>CII <sub>a</sub> ) | 25-28               | 4.63 m                        | - uc   | 0,7 m <sup>sest</sup>       | 1;93†   | 1,39 d                          |                 | 1.75 and 1.09 ( $H^6$ , $2H^7$ ), 1.32, 0.81 br.d and 0.78 hr d  |
|         |   |           | E, (exo-<br>CH <sub>3</sub> )   | 1/-17               | 4.57 d.qu                     | $1.53^{**}$  | 0,7 ***                     | 1,3 **  | 1,60 d                          |                 | $(2H^8, J_{\text{gem}} = 9.8), 1.04 \text{ d}$   |
|         |   |           | Z, (exo-<br>(CH <sub>3</sub> )  | 6-2                 | 4.6 ***                       | 1.7 **   | 0,7 ***                     | 1,78†   | 1,38d<br>/=1,2                  |                 | and 0.90 d (CH <sub>3</sub> , J = 6.7),<br>0.65-0.33 (CH <sub>2</sub> in cyclo-<br>C <sub>3</sub> H <sub>5</sub> )                                 |

| 2.44 and 2.22 m (H <sup>1</sup> , H <sup>3</sup> , H <sup>6</sup> ,<br>H <sup>8</sup> ), 2.26 m (H <sup>13</sup> -syn),<br>1.65 m (H <sup>2</sup> , H <sup>7</sup> ), 1.48 and<br>0.98 m (2H <sup>2</sup> , and 2H <sup>5</sup> ), 1.29 and<br>1.10 m (H <sup>12</sup> , H <sup>13</sup> ), 0.95%<br>(H <sup>12</sup> -syn in the Z-isomer),<br>0.91 m (H <sup>12</sup> -syn in the E-iso-<br>0.01 m (H <sup>2</sup> -syn in the E-iso- | $\begin{array}{cccccccc} (Cr_{2} & in & cyclo-C_{3}H_{5}) \\ (Cr_{2} & in & cyclo-C_{3}H_{5}) \\ 2.63 & (H^{4}, H^{7}), & 2.20 & br.6. \\ (H^{1}, H^{1}, 0), & 1.58 & and & 1.39 & br.d. \\ (H^{2}, H^{3}, H^{3}, H^{3}, H^{3}, H^{3}, 1^{-5}], & 1.51 \\ 1.82, & 1.30 & and & 1.21 & (H^{1}, 4, 1) \\ J_{gem} &= 10.5), & 0.6-0.35 & (Cr_{2}, 1) \\ in & cyclo-C_{3}H_{5}) \\ & in & cyclo-C_{3}H_{5}) \end{array}$ | J <sub>2</sub> . $e = 9.5$ ), 2.4 and 2.2 m (2H <sup>5</sup> , J <sub>2</sub> em = 17.5), 2.4 and 2.2 m (2H <sup>5</sup> , J <sub>2</sub> em = 17.5), 2.31 m (H <sup>1</sup> , H <sup>7</sup> ), 11.8 m (H <sup>11</sup> -ant1), 0.90 br.d (H <sup>11</sup> -syn, J <sub>2em</sub> = 10.4), 0.65-0.4 (CH <sub>2</sub> in cyclo <sup>-</sup> C.4 c) | 2.86 and 2.75 $m(H^1, H^8)$ ,<br>2.86 and 2.75 $m(H^1, H^8)$ ,<br>1.35-1.32 $(H^{-1})$ , the signals of<br>the other protons are overlapped by<br>the signals of the protons of<br>endo-XIV) | 2.67 and 2.21 m (H <sup>2</sup> , H <sup>5</sup> ), 2.43<br>and 1.76 m ( $2H^5$ ), 2.11 and 2.04<br>br.s (H <sup>1</sup> , H <sup>7</sup> in the Z-isomer),<br>2.08 and 1.99 br.s (H <sup>1</sup> , H <sup>7</sup> in the<br>E-isomer), 0.86 and 0.66 m<br>( $2H^{11}$ in the Z-isomer), 0.82 and | 0.70 m ( $2H^{-2}$ in the E-isometry,<br>0.58-0.43 ( $CH_2$ in cyclo- $C_3H_5$ )<br>The remaining signals were<br>not identified | _                |
|---|--|--|--|---|--|------------------|
|   | $\frac{5,96}{5,96}$  | 5,72<br>and<br>5,55 m<br>5,55 m<br>5,55 m  | 6,22<br>and<br>6,14 m<br>6,22<br>and   | 6,13 m<br>5,63 m<br>5,63 m<br>5,73 m  | 6,16<br>and<br>6,02 m  |                  |
| 1,58 d<br>/=1,3<br>1,38 d<br>/=1,4  | 1,62 d<br>J=1,4<br>1,40 d<br>J=1,4   | 1,60 d<br>1,38 d<br>1=1,2  | 1,58 d<br>/=1,2<br>1,47 d.d  | /=0,8<br>1,58 d<br>/=1,3<br>/=1,4<br>/=1,4  |  |                  |
| 1,75 1  | 4,31†<br>1,79**  | 1,31 m<br>1,80 †   | 1,43 †<br>1,81 †   | 1,27 m<br>1,77 †  |  |                  |
| 0.75 br,d<br>Jbc = 2.8<br>0.76 br,d<br>Jbc = 2.6  | 0,62 br.d<br>Jbc = 2.8<br>0,64 m   | 0,82 i<br>1.36 m<br>Jc. = 7.9<br>0,84 i<br>1.32 m  | **   | 0,9~0,6<br>0,9~0,6  |  | _                |
| 1.47%<br>L.87 d.t<br>Jab = 8.8<br>J <sub>bc</sub> = 2.6   | 1.61 d.t<br>Jbc = 2.8<br>1.82**  | 1,55 d.t<br>Jbc=2,7<br>1,77 d.t<br>Jbc=2,7   | 1,49 d.t<br>/bc=1,9<br>**  | 1,67 d.t.<br>Jbc = 2.7<br>1,90 d.t<br>Jbc = 2.7   |  | _                |
| 4.54 d.qu<br>Jab = 8.9<br>4.59 m<br>Jab~ 8.8  | J4.55 d.qu<br>Jab = 9.3<br>Jab = 9.1<br>Jab = 9.1  | 4,56 d.qu<br>/ab=9,2<br>/=1,2<br>4,61 m<br>/ =9,1  | 4,86 d.qu<br>Jab=8,1<br>1=1,2<br>4,88 m  | 4,56 d.qu<br>/ab=9,1<br>/=1,3<br>/,59 m<br>Jab = 8.6  | 4,88 m<br>/ ab~ 8  | -                |
| 60-63<br>37-10  | 6062<br>38-40  | 45-47<br>24-26   | 18-20<br>9-11  | 46-49<br>26-28  | 24-25  | е                |
| <u>3</u><br>87  | ,32<br>Z<br>Z  | ),27 <i>F</i><br>Z   | <u> </u>   | ,27 <i>E</i><br>Z   | E+Z  | n, eluent: hexan |
| 0,42 -0   | 0,25 (0  | 0,20-(   |  | 0,21-C  |  | ud 001-c         |
| 130–135<br>(0,8)  |  | 121–125<br>(0,8)   |  |   |  | 3el L, 4(        |
| (q X)   | (AIIb)   | endo-<br>(XIVb)  | endo-  | exo-<br>(XIVb)  | exo-<br>(XVb)  | *Silica {        |

\*\*The signal of the corresponding proton is overlapped by the signals of the other protons.

The signal of the methine proton in cyclo- $C_3H_5$  in all isomers is manifested as a broadened triplet of triplets with  $J_{cis} = 8.2^{-8}.6$ ,  $J_{trans} = 5.2^{-5.5}$  Hz, but in most cases it is partially overlapped by the signals of the other protons.

the presence of 0.5 mole %  $(PhCN)_2PdCl_2$ . In these conditions, as indicated in [8], only the strained intracyclic double bond is cyclopropanated, yielding exo-coupling of the cyclopropane fragment. According to the data from the PMR spectrum, product (VIb) also contained four isomers in the same ratio as in the starting (IIIb). However, the H<sup>b</sup> methine protons of the minor isomers are clearly manifested in the region of  $\delta$  2.62 and 2.85 ppm as a doublet of triplets with J<sub>bc</sub> = 2.7 Hz, due to the magnetic anisotropy of the cyclopropane ring, and this clearly indicates the anti configuration of the vinyl group



The ratio of isomers (IIIb) or (VIb), which is  $\4:1$  for exo:endo and  $\1.8:1$  for E:Z, was also determined based on the integral intensities of the signals of the corresponding protons.

In going from NBD to the other polycyclic hydrocarbons which contain a bicyclo[2.2.1] heptene fragment, a decrease is observed in the yields of the products of cross-cycloaddition and the selectivity of the reaction. The reaction of cyclopropene (Ib) with a fourfold molar excess of MNB, TCD, or PCT in the presence of 2-3 mole % (PhO)<sub>3</sub>P·CuCl yields a mixture of hydrocarbons containing both the products of [2 + 2] and the products of [1 + 2] cycloaddition, even at -20°C. Their yields decrease significantly with an increase in the molecular weight of the starting polycyclenes with a simultaneous increase in the degree of dimerization of (Ib) into (IVb) and (Vb).



It should be noted that the use of  $Ph_3P$ ·CuCl as the catalyst, by analogy with [3], results in the more selective occurrence of the reaction, which is virtually not accompanied by opening of the three-carbon ring. For example, the reaction of TCD with (Ia) in the presence of 3 mole %  $Ph_3P$ ·CuCl exclusively yields products of [2+2]-cycloaddition of (IVa) and (IXa), Cat = (PhO)\_3P·CuCl, and an olefin: (I) ratio of  $\sqrt{4}$ :1.

The products of cross-cycloaddition formed were initially separated from the starting substrates by vacuum distillation, and the adducts of [1+2]- and [2+2]-cycloaddition, which

are distinguished by the number of double bonds, were separated by preparative TLC, as in the case of the corresponding adducts (II) and (III). The structure and isomeric composition of the isolated structural isomers were established with the PMR spectrum in consideration of the multiplicity and multiplet character of the corresponding signals. By analogy with [2+2]-cycloadducts (II) [3], the presence of a narrow multiplet of H<sup>b</sup> protons and two singlets of protons from the CH<sub>3</sub> group in (IXb) and (XIb) at  $\delta$  0.55 and 1.2 ppm indicates the formation of exo-[2+2]-cycloadducts in the form of a mixture of syn and anti isomers (ratio of 1:1). The products of vinylcyclopropanation of (Xb) and (XIIb), which are structurally isomeric to them, are a mixture of two E- and Z-isomers according to the character of the H<sup>b</sup> and H<sup>c</sup> signals, in contrast to (IIIb) (ratio of  $\sim$ 1.5:1), with a pronounced exo, anti orientation of the vinylcyclopropane fragment (Table 2). In the case of MNB containing a mixture of endo- and exo-isomers ( $\sim$ 3.5:1), each of the hydrocarbons formed from syn- and anti-(VIIb) and E- and Z-(VIIIb) is again a mixture of two isomers according to the PMR spectra, caused by the isomerism of the CH<sub>3</sub> group in the norbornane fragment.

Addition of cyclopropenes to the norbornene double bond of polycyclenes (MNB, TCD, PCT) thus takes place with elevated stereoselectivity and results in obtaining the corresponding exo, trans isomers in the case of the adducts of [2+2]-cycloaddition and exo, anti-isomers in the case of adducts of [2+2]-cycloaddition. The partial formation of endo-isomeric products of vinylcyclopropanation of (III) is apparently only characteristic of NBD and is in agreement with its analogous behavior in some other reactions with unsaturated compounds [9].



We studied the catalytic reaction of (Ib) with DCPD to determine the regioselectivity and character of addition of cyclopropenes to polycyclenes with different double bonds in the molecule. Together with cyclodimer (IVb) and triene (Vb), isomeric pentacyclo[5.5.1.0<sup>2</sup>,<sup>6</sup>.  $0^{3}, 5.0^{8}, 1^{2}$ ]-9-tridecenes (XIIIb) are formed with both exo- and endo-DCPD in the presence of 1-1.5 mole % (PhO)<sub>3</sub>P·CuCl at -20°C with a yield of  $\sim$ 37%, and 9-vinyltetracyclo-[5.3.1.0<sup>2</sup>,<sup>6</sup>.0<sup>8</sup>, 1<sup>0</sup>]-3-undecenes (XIVb) and 4-vinyltetracyclo[6.2.1.0<sup>2</sup>, 7.0<sup>3</sup>, <sup>5</sup>]-9-undecenes (XIb) are formed with a total yield of 23-35%.

#### $Cat = (PhO)_3 P \cdot CuCI.$

The products of [2+2]- and [1+2]-cycloaddition were separated from triene (Vb) after vacuum distillation of the excess of DCPD and (IVb), separated by column chromatography (silica gel, eluent: hexane), and identified with the PMR spectra (250 and 500 MHz). As should have been expected, the PMR spectra of the cycloadducts of endo-(XIIIb) and exo-(XIIIb) are characterized by two sets of signals corresponding to the syn and anti-isomers ( $\sim$ 1:1), primarily indicated by the two singlet signals of protons from the CH<sub>3</sub> group in the region of  $\delta$  0.54 and 1.2 ppm. In addition, the appearance of signals of olefin protons at

TABLE 3. Properties of the Adducts of [2 + 2]-Cycloaddition of Cyclopropenes (Ia, b) to Polycyclenes

|                | Bp, °c                   |           |   |   | PMR spectrum**(C                                 | DCl3, ô, ppm, J, Ħ   | (2  |                                     |  |
|----------------|--------------------------|-----------|---|---|--|--|---|-------------------------------------|--|
| punod          | Hg)                      | TLC*', Rf | H <sup>a</sup> , Ha <sup>1</sup>  | Hb' Hb'   | H <sup>c</sup> , Hc <sup>1</sup>                 | рH   | н¢  | CH3                                 | other protons  |
| (IIa)          | 92 - 93                  | 0,40-0,46 |   |   |  |  |   |                                     | cf. [3]  |
| (911)          | 78-70                    | 0,39-0,46 |   |   |  |  |   |                                     | cf, [3]  |
| (IXa)          | 97–100<br>(1)<br>mp · 44 | 0,52-0,58 | 0,75 br.d<br>/ab~1,0<br>ab~   | 1,90 br.d   | 2,11 m<br>J.,2-exo=2,9                           | 2,38 d.t.<br>/de=9,1<br>/cd = 1,5                            | 1,13 .d. t,<br>$J_{de} = 9,1$<br>$J_{cf} = 1.5$     | 0,87 s<br>(änti)<br>1,15<br>(syn)   | 2,06 d.t (H <sup>3</sup> , H <sup>6</sup> , J <sub>3,4</sub> =4,2, $J=1,4$ ),<br>1,70 d.t (H <sup>2</sup> , H <sup>1</sup> , J <sub>1,2</sub> =2,9, J <sub>2,15</sub> =1,3),<br>1,41 m. (H <sup>4</sup> , H <sup>3</sup> -exc), 0,96 m (H <sup>4</sup> ,<br>H <sup>3</sup> -endo), J,31 d, qu and 0,82 d t (2H <sup>15</sup> ,   |
| †(4X1)         | 127-130                  | 0,50-0,58 | 0,72 m;<br>0,84 m'  | 1,91 br.s<br>2,15 br.s<br>J~1   | 2,07 m, 2,11 m                                   | 2,38 br.d,<br>2,42 br.d,<br>J <sub>de</sub> =9,6             | 1,11 d.t.<br>1,16 d.t.<br>Jde =9,6<br>J=1,5         | 0,55 s<br>(anti)<br>1,20s<br>(syn)  | $\begin{array}{l} \operatorname{gem}_{2(0)} \operatorname{Jost}_{1(2)} \operatorname{Jost}_{1(2)} \operatorname{Jost}_{1(2)} \operatorname{Jost}_{1(2)} \operatorname{Ins}_{1(2)} \operatorname{Hr}_{1} \operatorname{Jost}_{1(2)} \operatorname{Ins}_{1(2)} \operatorname{Jost}_{1(2)} \operatorname{Jost}_{1(2)} \operatorname{Jost}_{1(2)} \operatorname{Jost}_{2(1)} \operatorname{Jost}_{1(2)} \operatorname{Ins}_{1(2)} \operatorname{Jost}_{1(2)} \operatorname{Jost}_{1(2)} \operatorname{Ins}_{1(2)} \operatorname{Jost}_{1(2)} \operatorname{Ins}_{1(2)} \operatorname{Jost}_{1(2)} \operatorname{Ins}_{1(2)} $ |
| (d1b)          |                          | 0,35-0,40 | 0,90 m  | 1,93 br.s<br>2,14 br.s<br><i>J</i> ~1                                       | 2,04 m, 2,30 m                                   | 2,24 br.d<br>2,30 br.d<br>2,6 = 9,7<br>J <sub>de</sub> = 9,7 | 1,22 d.t,<br>1.24 d.t,<br>Jde = 9.7<br>J=1,4        | 0,54 s<br>(anti)<br>1,21 s<br>(syn) | cyclo-C <sub>3</sub> H <sub>5</sub> )<br>5,96 t (H <sup>3</sup> , H <sup>6</sup> , $J=2,0$ ), 2,63 m (H <sup>4</sup> ,<br>H <sup>3</sup> , 1,39 br. d (a 1,58 br. d (H <sup>2</sup> , H <sup>3</sup> ,<br>H <sup>3</sup> , H <sup>3</sup> , J $\sim$ 1,5), 1,81 m & 1,29 m<br>(2H <sup>3</sup> ), 1,11 m & 0,77 m (CH in cyclo-<br>G <sub>3</sub> H <sub>3</sub> ), 0,42 m, 0,21 m & -0,02 m (CH <sub>2</sub> in   |
| opue<br>(1111) | 118 - 123<br>(0,8)       | 0,31-0,38 | 0,75 d. d.<br>0,82 d. d.<br>0,98 d. d.<br>0,95 d. d.<br>1,88 d. d.                        | 1,60 d.d,<br>1,75 d.d,<br>1,83 d.d,<br>1,98 d.d,<br>1,98 d.d,<br>1,96 = 3.5 | 2,00 br.d,<br>2,04 br.d,<br>7,8~3,5 d,<br>2,18 m | 2,44 d.t<br>2,48 d.t<br>Jde = 9.5<br>7~1,5                   | 1,39 d.t,<br>1,41 d.t,<br><b>Jde</b> = 9.5<br>1~1,5 | 0,54 s<br>(anti)<br>1,18 s<br>(syn) | $\begin{array}{l} \begin{array}{l} \begin{array}{l} \begin{array}{l} \begin{array}{l} \begin{array}{l} \begin{array}{l} \begin{array}{l} $   |
| exo<br>(XIIIb) |                          | 0,300,37  | (ab) 1,0<br>()81 d.d.<br>()91 d.d.<br>()93 d.d.<br>()93 d.d.<br>Jab 2,4,4<br>Jab 21,5,4,4 | (100  | 1,77 m, 2,1 m                                    | 2,37 d.t<br>2,40 d.t<br>7de=10,0<br>7~1,5                    | 1,27 d.t,<br>1,31 d.t,<br>Jde = 10.0<br>J~1,5       | 0,53 s<br>(anti)<br>1,22 s<br>(syn) | 5,63 m (H <sup>10</sup> ), 5,43 m (H <sup>9</sup> ), 2,65 m and<br>2,2 m (H <sup>8</sup> , H <sup>12</sup> ), 2,49 m <b>6</b> , 1,86 m<br>(H <sup>11</sup> ), 1,05 m <b>6</b> ,0,82 m (CH in cyclo-<br>C <sub>3</sub> H <sub>5</sub> ), 0,41 m, 0,48 m <b>6</b> -0,02 m<br>(CH <sub>2</sub> in cyclo-C <sub>3</sub> H <sub>5</sub> )   |

\*Cf. note to table 2.

\*\*Assignment of the signals to the anti and syn isomers is difficult due to their approximately equal concentration in the

compounds formed.  $t^{13}C$  NMR spectrum ( $\delta$ , ppm): 50.31 and 50.36 ( $C^2$ ,  $C^7$ ), 43.42 and 43.56 ( $C^1$ ,  $C^8$ ), 38.26 and 38.35 ( $C^3$ ,  $C^6$ ), 36.53 and 36.55 ( $C^9$ ,  $C^{13}$ ), 35.59 and 36.55 ( $C^1^4$ ,  $C^{15}$ ), 31.31 ( $C^4$ ,  $C^5$ ), 24.21 and 28.36 ( $C^{10}$ ,  $C^{12}$ ), 22.47 and 23.0 ( $C^{11}$ ), 14.19 and 18.56 ( $CH_3$ ), 9.61 and 17.33 (CH in cyclo- $C_3H_5$ ), 1.52 and 2.0 ( $CH_2$  in cyclo- $C_3H_5$ ).

 $\delta$  5.6 ppm and their multiplet character, as well as the absence of signals at  $\delta$  6.1 ppm, clearly indicate the formation of [2 + 2]-cycloadducts exclusively at the norbornene multiple bond in DCPD. On the contrary, both double bonds of the starting dienes participate in the formation of [1+2]-cycloadducts, which also follows from the examination of the PMR spectra of the products of vinylcyclopropanation, for example, endo-(XIVb) and (XVb). Actually, the character of the signals of the olefin proton  $H^a$  and the protons of the  $CH_3$  group of the 2cyclopropylpropenyl fragment indicate the formation of four isomers, and each pair is determined by the E- and Z-isomerism of the 2-cyclopropylpropenyl fragment (E:Z  $\sim$  1.8:1). Information on the other pair of isomers was obtained based on the chemical shifts and multiplet character of the weak-field signals at  $\delta$  5.55-5.71 ppm characteristic of two nonequivalent olefin protons of the cyclopentene ring, and at  $\delta$  6.14-6.21 ppm, corresponding to the olefin protons of the norbornene fragment. The ratio of the integral intensities of these groups of signals, particularly for endo-(XIVb) and (XVb), is equal to ~2.5:1. Based on the ratio of the integral intensities obtained, the signals in the region of  $\delta$  4.56 and 4.61 ppm, which are in the form of a doublet of quintets with SSCC of  $J_{ab}$  = 9.2 Hz, correspond to the H<sup>a</sup> proton in E- and Z-endo-(XIVb), and the signals at  $\delta$  4.86 and 4.88 ppm with J<sub>ab</sub> = 8.1 Hz correspond to the H<sup>a</sup> proton in E- and Z-(XVb). Determination of the SSCC J<sub>ab</sub> permitted establishing the position of the  $\mathrm{H}^{\mathrm{b}}$  protons, manifested in the PMR spectrum in the form of a doublet of triplets, and determining the SSCC  $J_{bc}$ , equal to  $\sim 2.7$  Hz. This value of the SSCC, characteristic of trans protons in the cyclopropane fragment, indicates the anti orientation of the 2-cyclopropylpropenyl substituent in (XIVb) and basically also in (XVb).

The reaction of cyclopropene (Ib) with DCPD thus takes place like exo-[2+2]-cycloaddition exclusively at the strained double bond and as [1+2]-cycloaddition at each of the double bonds, but also primarily at the strained double bond of the norbornene fragment.

The features of the reaction of cyclopropenes with different double bonds are even more graphically manifested in the competitive reaction of (Ib) with an excess of an equimolar mixture of NBD and cyclopentadiene (CPD) conducted at -20°C in the presence of  $(PhO)_3 \cdot P$ CuCl. The product of [2+2]- cycloaddition of (IIb) is formed with NBD, and the product of [1+2]-cycloaddition, the corresponding bicyclo[3.1.0]-2-hexene [2] (ratio of  $\sim$ 4.3:1) is exclusively formed with CPD.

The results obtained show that the reaction of cyclopropenes with unsaturated compounds apparently takes place according to a coordinated mechanism in the coordination sphere of the metal without preliminary formation of vinylcarbene complexes. This is particularly confirmed by the different isomeric composition of 3-vinyltricyclo[ $3.2.1.0^2$ ,  $^4$ ]-6-octenes (XVI) formed in the catalytic reaction of NBD with cyclopropene or vinyldiazomethane (VDM). Both reactions are conducted in the same conditions at 0°C in the presence of  $\sim 1$  mole % CuCl and only differ with respect to the source of the C<sub>3</sub>H<sub>4</sub> fragment; only anti-isomer (XVI) is obtained with cyclopropene, and a mixture ( $\sim 1.3:1$ ) of anti and syn isomers of (XVI) is obtained with VDM [10].

## EXPERIMENTAL

The GLC analysis was conducted on an LKhM-iMD chromatograph with a flame-ionization detector and an I-02 integrator (300 × 0.3 cm columns with 5% SE-30, SP-2100, or Carbowax 20M on Chromaton N-AW-DMCS, 0.16-0.20 mm; helium was the carrier gas (30 ml/min). The PMR spectra were obtained for 5-10% solutions in CDCl<sub>3</sub> on Bruker WM-250 (250 MHz) and Bruker WP-500 (500 MHz) instruments; the chemical shifts are reported on the  $\delta$  scale relative to TMS as the internal standard.

3,3-Dimethyl- (Ia) and 3-methyl-3-cyclopropylcyclopropenes (Ib) were synthesized by selective monoreduction of the gem dibromocyclopropanes according to [11] and subsequent dehydrobromination of the corresponding 2-bromo-1,1-dialkylcyclopropanes [12]. 1,3,3-Trimethylcyclopropene (Ic) was prepared according to [13]. Norbornadiene (NBD) and its dimer (PCT), 5-methyl-2-norbornene (MNB), dimers of cyclopentadiene (DCPD) and exo,endo-tetracyclo[6.2.1.1<sup>3</sup>,  $60^2$ , 7]-4-dodecene (TPD) was vacuum distilled before use.

<u>Reaction of Cyclopropenes (Ia-c) with Polycyclic Unsaturated Hydrocarbons.</u> While stirring, 0.1-0.3 mmole of CuCl or  $(PhO)_3P$ ·CuCl (see Table 1 for NBD) was added to a solution of 10 mmoles of cyclopropene and 40-60 mmoles of unsaturated hydrocarbon in 5-8 ml of CH<sub>2</sub>Cl<sub>2</sub> in an atmosphere of Ar. A slight increase in temperature and the appearance of a greenish-brown coloring were observed. After 20-30 min, 10 ml of hexane was added to the mixture, it was filtered through a thin layer of silica gel, the solvent, the excess unsaturated hydrocarbon, and some of the dimers of cyclopropenes (IV) and (V) were distilled off [3]. The products of [1+2]- and [2+2]-cycloaddition (structural isomers) were subsequently separated by preparative TLC or column chromatography (silica gel L 40-100  $\mu$ m; eluent: hexane). The degree of separation of the structural isomers was monitored by GLC. The concentration of geometric isomers in each pair was estimated with the integral intensities of the corresponding signals in the PMR spectra. The results obtained are reported in Tables 2 and 3.

<u>Thermal Reaction of Cyclopropene (Ib) with NBD.</u> A mixture of 0.28 g (3 mmoles) of (Ib) and 2.8 g (30 mmoles) of NBD was heated in a sealed ampul for 15 min at 150°C. The subsequent vacuum distillation produced 0.5 g of a mixture of 4-methyl-4-cyclopropyl-exo,transtetracyclo[ $5.2.1.0^2, 6.0^3, 5$ ]-8-decene (IIb), anti-3-(2-cyclopropylpropen-1-yl)-exo- and endotricyclo[ $3.2.1.0^2, 4$ ]-6-octene (IIIb), and 3,6-dimethyl-3,6-dicyclopropyltricyclo[ $3.1.0.0^2, 4$ ]-hexane (IVb) (see Table 1), separated and analyzed as described above. According to the data in the PMR spectrum, the isomeric composition of [1 + 2]-cycloaducts of (IIIb) is identical to the analogous product obtained in the catalytic reaction of (Ib) and NBD.

Anti-3-(2-cyclopropylpropen-1-yl)-exo,exo- and endo,exo-tetracyclo[ $3.3.1.0^2, 4.0^6, 8$ ]nonane (VIb). Similar to [8], 0.56 g (93%) of (VIb), bp 92-96°C (1 mm), was obtained after vacuum distillation from 0.55 g (3 mmoles) of [1+2]-cycloadducts of (IIIb) in the presence of 10 mg of (PhCN)<sub>2</sub>·PdCl<sub>2</sub> and diazomethane generated from 1.0 g of N-nitroso-N-methylurea. The isomeric composition was established based on the PMR spectrum (See Table 2).

We would like to thank U. M. Dzhemilev for providing the samples of norbornadiene and its dimer, exo,trans,exo-pentacyclo[8.2.1.1<sup>4</sup>,<sup>7</sup>.0<sup>2</sup>,<sup>9</sup>.0<sup>3</sup>,<sup>8</sup>]-5,11-tetradecadiene.

### CONCLUSIONS

1. The reaction of 3,3-disubstituted cyclopropene hydrocarbons with norbornadiene in the presence of 1-3 mole % CuCl or  $(PhO)_3P$ ·CuCl at 0-40°C takes place according to the scheme of both [2+2]- and [1+2]- cycloaddition with the formation of the corresponding exo,trans-tetracyclo $[5.2.1.0^2, 6.0^3, 5]$ -8-decenes and 3-vinykltricyclo $[3.2.1.0^2, 4]$ -6-octenes with a total yield of 70-90%, and the yield of the latter increased with an increase in the temperature in going from  $(PhO)_3P$ ·CuCl to CuCl.

2. The reaction of 3-methyl-3-cyclopropylcyclopropene with more complex polycyclic hydrocarbons containing a bicyclo[2.2.1]heptene fragment takes place less efficiently and less selectively than with norbornene, and yields a mixture of products of [1+2]- and [2+2]- cycloaddition with a yield of 30-65% and significant dimerization of the starting cyclo-propene in the presence of  $(PhO)_{3}P$ ·CuCl even at -20°C.

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