BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3147—3149 (1972)

Syntheses of Isoprenoids from Isoprene. III. The Dimerizations of Dimethylcyclopropanes[1)]

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(Received December 27, 1971)

1,1-Dimethylcyclopropane(I) was found to dimerize selectively by the action of boron trifluoride etherate. In the products, compound (III), which had been presumed, and the reaction intermediates (VII and VIII) were identified. The reaction mechanism was discussed. 1,2-Dimethylcyclopropane(VI) gave the same products.

1,1-Dimethylcyclopropane(I) has been reported to polymerize.[2-4)] However, the oligomers have not been studied in detail. We will reported here, however, that I is dimerized selectively by the action of boron trifluoride etherate to give 3,4,5,5-tetramethyl-2-hexene(II), 2,3,4,4-tetramethyl-1-hexene(III), 3,5,5-trimethyl-2-heptene(IV), and 3,4,4,5-tetramethyl-2-hexene(V). Furthermore, the reaction intermediates were confirmed, and the reaction mechanism was discussed. 1,2-Dimethylcyclopropane(VI) was also reacted by the same catalyst.

1) Part II: J. Tanaka, T. Katagiri, and T. Hirabayashi, *Nippon Kagaku Zasshi*, **88**, 1106 (1967).

2) H. Pines, W. D. Huntsman, and V. N. Ipatieff, *J. Amer. Chem. Soc.*, **75**, 2315 (1953).

3) A. D. Ketley, *J. Polym. Sci., Part B*, **1**, 313 (1963).

4) S. Aoki, Y. Harita, T. Otsu, and M. Imoto, This Bulletin, **39**, 889 (1966).

Experimental

Materials. 1,1-Dimethylcyclopropane(I) was synthesized from isoprene by our method.[5)] Bp 21°C, NMR(τ); 8.97(6H, s), 9.80(4H, s). 1,2-Dimethylcyclopropane(VI) was prepared from 2-butene by a modification of Doering and Hoffmann's method.[6)] Bp 28—37°C, NMR(τ); 9.00(d), 9.01(d), 9.20—9.91(m).

Measurements. The products were analyzed after glc fractionation (15% Apiezon grease L/Celite 545, 4 mmϕ $\times$2.5 m, H_2: 45ml/min, 90°C). The IR spectra were recorded on a Perkin Elmer Model 337 infrared spectrophotometer. The NMR spectra were run on a Hitachi-Perkin Elmer Model R-20 (60 MHz) spectrometer, using tetramethyl-

5) J. Tanaka, T. Katagiri, and K. Takabe, *Yuki Gosei Kagaku Kyokai Shi*, **28**, 763, 764 (1970).

6) W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, **76**, 6162 (1954).

TABLE 1. THE REACTIONS OF 1,1-DIMETHYLCYCLOPROPANE (I) AT THE DIFFERENT TEMPERATURES[a)]
(I: 2 g, $BF_3 \cdot O(C_2H_5)_2$: 1 g, one hour)

Temp. (°C)	Yield (%)	Dimer (%)	Products (%)				
			II	III	IV	V	Others
−17	10	94	4	65	trace	22	9
−7	22	94	4	55	7	23	11
0	40	92	7	27	9	46	11
5	52	91	12	21	9	43	15
14	70	88	34	7	9	33	17

a) In the NMR spectra of the volatile fraction of the reaction mixtures, the signals at τ 8.30—8.50(m), τ 5.40(s), and τ 4.86(q) were noted. The first signal came from methyl groups, the second came from VII, and the third came from VIII.

TABLE 2. THE REACTIONS OF 1,1-DIMETHYLCYCLOPROPANE(I) FOR THE VARIOUS PERIODS
(I: 2 g, $BF_3 \cdot O(C_2H_5)_2$: 1 g, 0°C)

Period (hr)	Yield (%)	Dimer (%)	Products (%)				
			II	III	IV	V	Others
0.5	30	93	6	31	10	40	13
1	40	92	7	27	9	46	11
3	55	83	17	13	16	36	18

TABLE 3. THE REACTIONS OF 2-METHYLBUTENES(VII/VIII=6/1) AND 1,2-DIMETHYLCYCLOPROPANE(VI)
(Reactant: 2 g, $BF_3 \cdot O(C_2H_5)_2$: 1 g)

Reactant	Temp. (°C)	Period (hr)	Yield (%)	Dimer (%)	Products (%)				
					II	III	IV	V	Others
VII and VIII	−17	0.15	74	99	0	72	11	12	5
VII and VIII	−17	0.5	81	95	0	68	10	18	4
VII and VIII	−17	1	90	93	2	54	10	27	8
VII and VIII	−7	1	90	93	38	5	13	29	15
VII and VIII	0	1	91	87	48	3	21	9	19
VII and VIII	20	1	90	70	52	3	21	6	18
VI	22	1	17	93	6	56	10	20	8
VI	22	3	28	89	43	8	13	22	14

silane as the internal reference and carbon tetrachloride as the solvent, at an ordinary temperature. The mass spectra were recorded on a Hitachi RMU-7U mass spectrometer.

Procedure. In a 30-ml flask, which was controlled at a fixed temperature, we placed 2 g of I, and then 1 g of boron trifluoride etherate was stirred on, drop by drop. After the reaction, the catalyst was deactivated with water and the reaction mixture was extracted with ether. The ether layer was washed with a saturated NaCl aqueous solution and dried over K_2CO_3. VI was reacted in the same manner.

3,4,5,5-Tetramethyl-2-hexene(II). RT: 10.5 min. IR(cm^{-1}): 1670, 820. Mass(*m/e*): 140(M^+, 22%), 84 ($M^+-C_4H_9$, 100%), IR(cm^{-1}): Mass(*m/e*): 140($M^+-C_4H_9$, 1670, 820. 100%), 57($C_4H_9^+$, 60%). NMR(τ): 4.89(1H, q, J=6.0 Hz), 8.09(1H, q, J=6.8 Hz), 8.45(3H, s), 8.49 (3H, d, J=6.0 Hz), 9.04(3H, d, J=6.8 Hz), 9.16(9H, s). n_D^{20} 1.4377(lit,[7)] n_D^{20} 1.4360).

2,3,4,4-Tetramethyl-1-hexene(III). RT: 12.5 min. IR(cm^{-1}): 1650, 890. Mass(*m/e*): 140(M^+, 2%), 70($C_5H_{10}^+$, 100%), 43($C_3H_7^+$, 77%). NMR(τ): 5.23(1H, s), 5.39(1H, s), 7.94(1H, q, J=7.0 Hz), 8.30(3H, s), 8.81(2H, q, J=7.0 Hz), 9.03(3H, d, J=7.0 Hz), 9.19(3H, t, J=7.0 Hz). n^{20} 1.4389.

3,5,5-Trimethyl-2-heptene(IV) and 3,4,4,5,-Tetramethyl-2-hexene(V). IV and V had the same RT (14.0 min) and could not be identified. Therefore, these two compounds were confirmed after an ozonolysis of the glc fraction (RT: 14.0 min) carried out in chloroform. *3,3,4-Tetramethyl-2-pentanone*[8)] (which was derived from V). RT: 12.9 min. IR(cm^{-1}): 1710. NMR(τ): 7.79(3H, s), 7.75—8.50(1H, m), 9.02(6H, s), 9.18(6H, d, J=6.8 Hz). *4,4-Dimethyl-2-hexanone* (which was derived from IV). RT: 11.7 min. IR(cm^{-1}): 1710. NMR(τ): 7.77(2H, s), 7.99(3H, s), 8.75(2H, q, J=6.8 Hz), 9.07(6H, s), 9.07(3H, t, J=6.8 Hz).

Results and Discussion

The yields of IV were not seriously affected by the reaction periods or times, as is shown in Tables 1 and 2. Therefore, the reaction path to produce IV seems to

7) F. C. Whitmore and A. Mosher. *J. Amer. Chem. Soc.*, **63**, 1120 (1941).

8) This compound was identical with the authentic sample synthesized by the method of the literature (J. W. Baker, *J. Chem. Soc.*, **1950**, 1302.

be different from the path to give other dimers, such as II, III, and V. Furthermore, the components in the volatile fraction of the reaction mixture were confirmed to be 2-methyl-2-butene(VII) and 2-methyl-1-butene (VIII). Since these seemed to be the reaction intermediates, mixtures of these compounds obtained from *t*-amyl alcohol by dehydration (VII: VIII=6 : 1) were reacted by the same catalyst. The results (Table 3) were very similar to those for I, while the reactivity to the dimers was superior to that of I.

From these results, the mechanism to produce II, III, V, and IV may be as follows. The cation(IX) formed from I was deprotonated to give VII and VIII, and then coupled with VII to give the cation(X). From this cation, III was obtained by deprotonation. The formation of II and V from the cation(X) can be explained by the mechanism of the carbonium-ion rearrangements:[9-11] these rearrangements were clarified by the reaction of III.[12] That is, the confirmation of III clarified the existence of X predicted by Whitmore and Mosher.[9] The other dimer, IV, was formed through the cation(XI), which was formed by the coupling of the above-mentioned cation (IX) and VIII.

Since scarcely VII and VIII could be obtained in the reaction of III,[12] the two reaction paths seem to be largely independent. The reaction scheme is illustrated in Fig. 1.

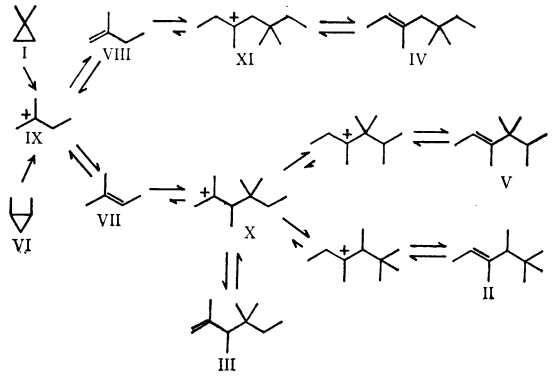

Fig. 1. The reaction scheme.

When 1,2-dimethylcyclopropane(VI) was reacted by the same catalyst (Table 3), the results were very similar to those for I, but the reactivity was inferior to that of I. The difference in the reactivities may be due to the relative difficulties of the cleavage of the cyclopropanes.[13,14]

9) F. C. Whitmore and W. A. Mosher, *J. Amer. Chem. Soc.*, **68**, 281 (1946).
10) A. Schneider and R. M. Kennedy, *ibid.*, **73**, 5017 (1951).
11) G. J. Karabatsos, F. M. Vane, and S. Mayerson, *ibid.*, **85**, 733 (1963).
12) When III was reacted by boron trifluoride etherate at 37°C for one hour, the C_{10} fraction was obtained in a 95% yield; its composition was II (37%), III (15%), and V (35%).
13) O. E. Nesmeyanova, M. Yu. Lukina, and B. A. Kazanskii, *Dokl. Akad. Nauk SSSR*, **153**, 357 (1963).
14) M. Yu. Lukina, O. A. Nesmeyanova, G. A. Khotimskaya, V. A. Ovodova, and B. A. Kazanskii, *ibid.* **158**, 652 (1964).