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A Simple Preparation of 2,3-Dimethylenebicyclo[2.2.1]hept-5-ene

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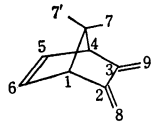
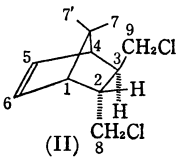
2,3-Dimethylenebicyclo[2.2.1]hept-5-ene (I) is a compound possessing an interesting triene system and can be used as a starting material to synthesize many other polycyclic compounds. This compound was already synthesized by Alder and his co-workers;[1] however, their procedure contained multi-step of reactions and seems not to be suitable for large scale preparation. We have been interested in the chemistry of this triene compound and found a simple preparation method of I which was composed of two step reactions. This procedure is presented in this report.

Diels-Alder reaction of cyclopentadiene and *trans*-1,4-dichlorobut-2-ene gave *trans*-2,3-dichloromethyl-bicyclo-[2.2.1]hept-5-ene (II) accompanied with small amounts of isomeric products of II. Dehydrochlorination of II by Hock's method[2] which had been successfully applied to dehydrohalogenation of analogous compounds resulted in the recovery of the starting substance. After several fruitless trials, we found that treatment of II with potassium hydroxide in DMSO afforded the desired compound in 55—65% yield.



(I)



(II)

NMR spectra of I and II are shown in Table 1. The assignment of all hydrogens of I and II was done by double and triple resonance technique. H_7 of I shows a long-range coupling with H_5 and H_6 which nicely accords with W-rule[3] and this type long-range coupling is also observed between H_1 and H_5 (H_4 and H_6). The coupling constants ($J_{1,2}$ and $J_{3,4}$) of II can be explained from the fact that the dihedral angle between H_1 and H_2 and that between H_3 and H_4 are nearly 45° and 90° respectively, which values are agree with those of the Dreiding model of II. It should be noted that the spectrum indicated non-equivalency of methylene hydrogens of C_8 and C_9.

The mass spectrum of II shows a very intense peak at mass 66 and other peak's intensities are less 1/10 than that of the peak at 66: *m/e* (relative intensities); 190 (parent, 1.40), 105 (1.68), 91 (1.12), 67 (66+1, 6.20), 66 (M–$C_4H_6Cl_2$, 100), and 54 (1.07). The ratio of the intensities of the isotope peaks of the parent ion nicely accords with the reported values:[4] *m/e* (relative intensities); 190, 192, and 194 (100, 65, and 10). Therefore, *retro*-Diels-Alder type reaction is the most significant fragmentation of electron impact of II. On the other hand, the mass spectrum of I is as follows: *m/e* (relative intensities); 118 (parent, 76), 117 (M-1, 100), 103 (M–CH_2, 11), 91 (117-C_2H_2, 21), 78 (10), and 66 (M–C_4H_4, 61). In this case, a hydrogen was probably taken off from the methylene bridge and the base peak was formed. Although the main fragmentation is also *retro*-Diels-Alder type one, the intensity of mass 66 peak is not strong compared with that in the case of II. The reason of this may be due to the formation of unfavorable cummulene fragment. This property is parallel with thermally stable nature of I.[5]

Experimental[6]

trans-2,3-Dichloromethyl-bicyclo[2.2.1]hept-5-ene (II) A mixture of 8.26 g of 1,4-dichloro-2-butene, 5.26 g of freshly distilled cyclopentadiene and 6 m*l* of benzene in a sealed glass tube was heated in an autoclave which was also filled with benzene. An oil bath (or electric heater) used should be

TABLE 1[a]. δ values of the products (I and II)

	H_1	H_2	H_3	H_4	H_5	H_6	H_7	$H_{7'}$	H_8	H_9
I	2.23			3.23	6.11	6.11	1.56	1.73	4.87	4.87
									5.06	5.06
II	2.99	2.04	1.30	2.79	6.27	6.10	1.51	1.51	3.11	3.63
									3.40	4.45

J values of the products (I and II)

	$J_{1,2}$	$J_{1,5}$	$J_{1,6}$	$J_{1,7}$	$J_{2,3}$	$J_{2,8}$	$J_{3,4}$	$J_{3,9}$	$J_{4,5}$	$J_{4,6}$	$J_{4,7}$	$J_{5,6}$	$J_{5,7}$	$J_{6,7}$	$J_{7,7'}$	$J_{8,8'}$	$J_{9,9'}$
I		1.4	1.4	1.6					1.4	1.4	0		0.5	0.5	8.5	~0.3	~0.3
II	3.5	0	3.5	1.0	5.0	10.5	~0	6.5	3.5	~0	1.5	5.5	~0.3	~0.3		9.5	10.5

a) All chemical shifts are presented by ppm from internal standard TMS in CCl_4 at 100 MHz, and all coupling constants are presented by Hz.

1) K. Alder, S. Hartung, and O. Netz, *Chem. Ber.*, **90**, 1 (1957).
2) P. E. Hock and J. M. Clegg, *J. Amer. Chem. Soc.*, **81**, 5413 (1959).
3) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).
4) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley & Sons, New York (1963), p. 17.
5) When I was heated up to 500°C in vapor phase, I was recovered almost quantitatively; unpublished work.
6) All boiling points are uncorrected.

heated at 180°C before the reaction and the temperature should be kept at 180±5°C during the reaction. After cooling, the benzene was removed under reduced pressure and then the residue was distilled fractionally. II was obtained as a colorless oil (7.35 g), bp 117°C/16 mmHg; average yields of II are 50—60%. ν (oil neat); 3070, 2960, 2905, 1460, 1445, 1325, 1285, 1265, and 710 cm^{-1}.

Found: C, 56.84; H, 6.50%. Calcd for $C_9H_{10}Cl_2$: C, 56.56; H, 6.33%.

2,3-Dimethylenebicyclo[2.2.1]hept-5-ene (I). A solution of 6.65 g of II and 7.0 g of potassium hydroxide in 30 m*l* of DMSO which contained 3 m*l* of water was put in a Claisen flask and heated for 6 hr at 160±5°C under gentle stream of nitrogen. As the reaction proceeded, oily products were distilled out and collected in an flask cooled in an ice bath. The collected products were washed well with water, extracted with ether, and the combined ether layers were dried over sodium sulfate. After the drying reagent and the ether had been removed, the obtained products were distilled fractionally to give 2.63 g of I; bp 142°C (lit, bp 142°C);[1] average yields of I are 55—65%. λ_{MeOH}^{max}; 242 mμ (log ε, 3.97). ν (oil neat); 3060, 2957, 2855, 1640, 1420, 1308, 880, 792, 765, and 678 cm^{-1}.

The oily product afforded an adduct, mp 121°C, in 95% yield on reacting with maleic anhydride.

The mass spectra were measured at 70 eV by indirect method.

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