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Utilizing Emulsification in the Synthesis of Dihydro-*exo*-dicyclopentadienyl Ethers and Their Esters

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Synopsis. Alcohols and carboxylic acids were subjected to an addition reaction with dicyclopentadiene, using dodecylbenzenesulfonic acid both as the emulsifying agent and the acid catalyst. Dihydro-*exo*-dicyclopentadienyl ethers and their esters were syntheized in good yields and found to be free of undesirable side reactions.

It is important to investigate the method of synthesizing dicyclopentadienyl ethers and their esters because of the usefulness of these compounds as plasticizers and drying oils. There are two known methods for preparing these compounds. One involves the reaction of a carboxylic acid with hydroxy-dihydro-*exo*-dicyclopentadiene and an alkaline metal alcoholate with dihydro-*exo*-dicyclopentadienyl halide.[1] The other method consists of an electrophilic addition reaction[2] of dicyclopentadiene with an alcohol or a carboxylic acid by using the difference in the reactivities[3] of the two double bonds in dicyclopentadiene in the presence of an acid catalyst, although the yields for this method are generally low.

The present paper describes an alternative method of preparing these compounds with a view to obtaining satisfactory yields. The necessary procedures are also dealt with.

Results and Discussion

Bruson *et al.* have reported on the preparation of dihydro-*exo*-dicyclopentadienyl ether[4] by the electrophilic reaction of an alcohol with dicyclopentadiene, and of dihydro-*exo*-dicyclopentadienyl ester by a similar reaction involving a carboxylic acid with dicyclopentadiene.[5]

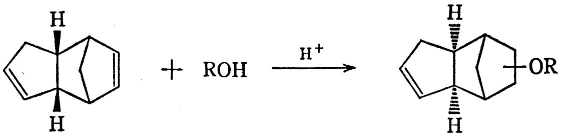
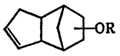


Table shows the results of this experiment. It is noted that the amount of acid catalyst required in the reaction of dicyclopentadiene with a carboxylic acid is rather small in comparison with that in the reaction of dicyclopentadiene with an alcohol, since in the former case it is needed only as a co-catalyst. As can be readily seen, both alcohols charaterized by poor or no solubility in dicyclopentadiene, as well as carboxylic acids, gave the addition products in very low yields. It is assumed that the most important cause of the limited yields in the heterogeneous system is due to the poor or no solubility of these compounds in dicyclopentadiene. In particular, the heterogeneous system causes side reactions *i.e.*, partial cationic polymerization[6] of dicyclopentadiene or a dehydratic condensation reaction[7] of alcohol in the presence of concentrated sulfuric acid.

To avoid this and to increase the yield, it was thought that a compound that would homogenize the heterogeneous system and at the same time act as a catalyst for the reaction would be worth testing. The refore, use was made of dodecylbenzenesulfonic acid, a strong acid capable of emulsifying action. The results show that the emulsifying action homogenized the heterogeneous system and restrained side reactions at the same time, thus increasing the yield and permitting the use of

Table 1. Results of the preparation of dihydro-*exo*-dicyclopentadienyl ethers and their esters

	 R	Solubility of ROH in dicyclopentadiene	Run A (98% H_2SO_4) Run B ($C_{12}H_{25}C_6H_5$-SO_3H) Amount of catalyst[a] (mol)	Yield[b] (%)	Bp (°C/Torr)	Found (Calcd %)			IR (cm^{-1})	NMR[8-10] (ppm)	Mass $(m/e)^+$
						C	H	O			
1a	CH_3	poor (hetero)[c]	A 0.25 B 0.05	31 81	96—98/12—13	80.71 (80.44)	9.80 (9.83)	9.49 (9.74)	1610 1100	3.1 (3H, CH_3) 3.15(1H, H_8)	164 15
1b	CH_2CH_2OH	insoluble (hetero)	A 0.3 B 0.05	16 76	105—106/0.5	74.05 (74.19)	9.23 (9.34)	16.72 (16.47)	1615 1100	2.72(1H, OH) 3.4 (1H, H_8) 3.45, 3.65 (4H, $-CH_2-$)	194 45
1c	C_6H_5	good (homo)[d]	A 0.3 B 0.05	20 79	121—122/1	85.12 (84.19)	8.15 (8.02)	6.73 (7.07)	1610 1600 1500 1250	4.1 (1H, H_8) 6.6—7.2 (5H, C_6H_5)	226 77
2a	$OCCH_3$	good (homo)	A 0.05 B 0.04	61 82	96—97/5	74.83 (74.97)	8.21 (8.39)	16.96 (16.64)	1730 1620 1250	1.9 (3H, CH_3) 4.6 (1H, H_8)	192 43
2b	$OCCH=CH_2$	good (homo)	A 0.05 B 0.04	62 85	131—132/7	76.32 (76.44)	7.81 (7.90)	15.87 (15.67)	1725 1630 1600 1200	4.65(1H, H_8) 5.8—6.3 (3H, $CH=CH_2$)	204 55
2c	OCC_6H_5	poor (hetero)	A 0.2[e] B 0.04	19 63	158—159/1	80.10 (80.28)	7.02 (7.13)	12.88 (12.58)	1720 1610 1600 1500 1280	4.9 (1H, H_8) 7.4, 8.0 (5H, C_6H_5)	254 105

a) The amount of the catalyst was calculated on the basis of one mol of dicyclopentadiene. b) Given in the ratio of the percentage of the amount obtained from GLPC (without **1c** and **2c** isolated) to that calculated from the mol of dicyclopentadiene used. c) Heterogeneous system in the reaction. d) Homogeneous system in the reaction. e) BF_3OEt_2 was used.

smaller amounts of the acid catalyst. From the above data, it was concluded that an acid with emulsifying action and capable of catalyzing the reaction, such as dodecylbenzenesulfonic acid, gives the addition product in better yields for carboxylic acids, as well as for alcohols, even when these are poorly soluble or insoluble in dicyclopentadiene.

Experimental

The NMR spectra were recorded on a Nippon Denshi Kogaku Model JNM-4H-100 spectrometer in parts per million (ppm) from internal tetramethylsilane. The IR spectra were obtained on a Nippon Bunko Model DS-701 D spectrometer using neat liqids between KBr disks. The mass spectra were measured on a Nippon Denshi Model D-100 spectrometer with an electron bombarding energy of 75 eV.

*Preparation of Ethylene Glycol Mono(dihydro-*exo*-dicyclopentadienyl) Ether.* Dodecylbenzenesulfonic acid (8.15 g, 0.025 mol) was added dropwise to the stirred ethylene glycol (31 g, 0.5 mol) at room temperature. The dicyclopentadiene (66 g, 0.5 mol) was added dropwise and the mixture was rapidly stirred until it was emulsified. The emulsified mixture was then heated to 100 °C and the reaction proceeded for 4 h. The reaction mixture was cooled to room temperature and benzene (100 g) was added to the stirred mixture. The mixture was poured into 3% aqueous sodium chloride (500 g) containing sodium hydroxide (1.4 g, 0.035 mol) to neutralize the acid, and left standing to separate out the oil layer. The layer was washed four times with a portion of 3% aqueous sodium chloride (500 g), dried over sodium sulfate, and distilled *in vacuo*. Bp 105—106 °C/0.5 Torr, Yield: 76% (from GLPC).

*Preparation of Dihydro-*exo*-dicyclopentadienyl Acetate.* Dodecylbenzenesulfonic acid (6.5 g, 0.02 mol) was added slowly to acetic acid (30 g, 0.5 mol), and cooled to 10 °C, followed by dropwise addition of dicyclopentadiene (66 g, 0.5 mol). The stirred mixture was heated to 100 °C and allowed to react for 5 h. The reaction mixture was cooled to room temperature, ethyl ether (100 g) was added and the mixture was poured into water (500 g) to separate out the oil layer. The oil layer was neutralized with sodium carbonate, washed a few times with a portion of water (500 g), dried over sodium sulfate, and vacuum distilled. Bp 96—97 °C/5 Torr, Yield: 82% (from GLPC.).

Preparation of the addition products using other alcohols or carboxylic acids was similar in principle to the procedure described above.

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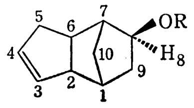
8) The chemical shifts of the protons of dihydro-*exo*-dicyclopentadienyl derivatives are more complicated at high fields (1.2—2.7 ppm). However, these chemical shifts were assigned from the data based on Refs. 9 and 10. Each proton of the dihydro-*exo*-dicyclopentadienyl group is numbered as follows:



(or OR at C_9) R=Alkyl or acyl group

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