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The Synthesis of 3-Substituted Tropilidenes by the Dehydration of 1-Substituted 2,6-Cycloheptadienols. A New Unambiguous Route

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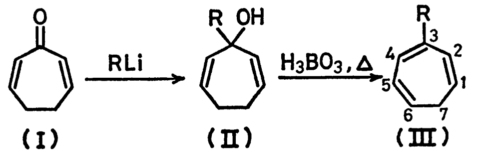
Synopsis. 3-Alkyl-, 3-aryl-, and 3-deuteriotropilidenes are prepared in 21—29% yields by the dehydration of the corresponding 1-substituted 2,6-cycloheptadienols with boric acid. The present method provides an unambiguous route to the title compounds.

Several methods have been proposed for the synthesis of 1-, 2-, or 3-substituted tropilidenes. The relatively simple ones include: (a) the reaction of substituted tropylium ions with metal hydrides,[1] (b) the thermal[2] or photochemical[3] isomerization of 7-substituted tropilidenes, and (c) the ring-expansion of aromatic compounds with carbene.[4] However, such methods generally afford a mixture of isomeric substituted tropilidenes which are separated from each other only with considerable difficulty because of the similarity of the boiling points. Previously we reported an unambiguous route to 3-alkyl-2,4-dimethyltropilidenes which involves the addition of alkyllithiums to 2,7-dimethyl-2,6-cycloheptadienone and the subsequent dehydration of 1-alkyl-2,7-dimethyl-2,6-cycloheptadienols in the presence of boric acid.[5] In the present work the method has been applied to 2,6-cycloheptadienone (I), utilizing lithium aluminum deuteride or various alkyl- and phenyllithiums, in the hope of exploring a selective route to 3-substituted tropilidenes (III) (Eq. 1).



(1)

The alcohols (II) were obtained in approximately quantitative yields except for the cases of R=*i*-Pr or *t*-Bu.[6] The dehydration of the crude alcohols with boric acid,[7] followed by a single distillation, afforded 3-substituted tropilidenes (III) in a greater than 96% purity. The results of the synthesis are shown in Table 1. Although the yields of III are generally low (21—29%) because of the formation of polymers during dehydration, the excellent purity of the tropilidenes permits the use of the method applicable to the unambiguous synthesis of III. It should be noted that the present method provides a unique route to highly pure tropilidene-3-*d*, which has never been accessible by any other methods.

For comparison, the dehydration of 1-methyl-2,6-cycloheptadienol with boric anhydride, oxalic acid, or potassium bisulfate was examined. It was found that boric anhydride works much like boric acid, whereas oxalic acid and potassium bisulfate give 3-methyltropilidene in a purity of 89% in each case, the impurities being difficult to separate by repeated distillations.

TABLE 1. RESULTS OF THE SYNTHESIS OF 3-SUBSTITUTED TROPILIDENES

Lithium compound	3-Substituent	Yield[a] %	Purity %	Boiling point °C (Torr)
$LiAlH_4$	H	24	—	115—116
$LiAlD_4$	D	29	100[b]	115—116
MeLi	Me	25	96[c,d]	45— 48 (21)
i-PrLi	*i*-Pr	21	97[c,d]	99—100 (50)
c-PrLi	*c*-Pr	24	97[c,d]	58— 62 (70)
PhLi	Ph	29	99[c,d]	137—139 (3)

a) Overall isolated yield. b) Determined by NMR. c) Determined by GLC. d) Preparative GLC is required for further purification.

The extension of the present method to the selective synthesis of 1-substituted tropilidenes was attempted starting with 3,5-cycloheptadienone, but such an application was found not to be straightforward, since 3,5-cycloheptadienone, when treated with methyllithium, afforded the corresponding alcohol in a low yield (31%) and the rest of the starting ketone was recovered unchanged. Presumably the enolization of 3,5-cycloheptadienone is preferable to the addition reaction in the presence of methyllithium.

The present method has been successfully applied to the preparation of mixtures of isomeric disubstituted tropilidenes as the precursors of 1,2-disubstituted tropylium ions; the work will be reported elsewhere, together with the results of the one-electron reduction of substituted tropylium ions with chromium (II).[8]

Experimental

Materials. 2,6- and 3,5-Cycloheptadienones were prepared by the procedure of Garbisch.[9]

1-Substituted 2,6-Cycloheptadienols (II). 2,6-Cycloheptadienone was treated with a 30% excess amount of the appropriate lithium compound in anhydrous ether at 0—20 °C, except that the reaction with *t*-butyllithium was conducted at −72 °C. For isopropyllithium, pentane was used in place of ether as the solvent.[10] The NMR spectra of the crude product showed that all the lithium compounds, except for isopropyl- and *t*-butyllithium, gave the expected alcohols (II) in approximately quantitative yields. Isopropyllithium afforded a mixture composed of the expected alcohol and unidentified ketones, which were presumably formed by the 1,4-addition reaction. A detailed characterization of the products has not been carried out. *t*-Butyllithium failed to give 1-*t*-butyl-2,6-cycloheptadienol, as demonstrated by the IR spectrum of the crude product; instead, it afforded a mixture of unidentified ketones and ether-insoluble polymers.

Table 2. NMR spectra of 3-substituted tropilidenes

3-Substituent R	δ, ppm CCl_4, 60 MHz)							Coupling constant, Hz	
	H-1	H-2	H-4	H-5	H-6	H-7	R		
D	5.25	6.12	6.48	6.05	5.25	2.20	—	$J_{1,2}=J_{5,6}=9.0$ $J_{4,5}=3.0$	$J_{1,7}=J_{6,7}=6.4$
Me	≈5.20	5.92	6.28	5.97	≈5.20	2.17	2.03 s	$J_{1,2}=J_{5,6}=9.2$ $J_{4,5}=6.0$	$J_{1,7}=J_{6,7}=6.2$
i-Pr	≈5.23	6.02	6.32	6.00	≈5.23	2.15	1.10 d 2.50m	$J_{1,2}=J_{5,6}=9.2$ $J_{4,5}=6.0$	$J_{1,7}=J_{6,7}=6.6$
c-Pr	≈5.15	5.75	6.21	5.89	≈5.15	2.12	0.63m 1.57m	$J_{1,2}=J_{5,6}=9.0$ $J_{4,5}=6.0$	$J_{1,7}=J_{6,7}=6.0$
Ph	≈5.37	6.28	6.80	6.17	≈5.37	2.25	7.25m	$J_{1,2}=J_{5,6}=8.6$ $J_{4,5}=6.0$	$J_{1,7}=J_{6,7}=7.0$

In each case the crude product was used in the dehydration step without further purification.

Dehydration of 1-Substituted 2,6-Cycloheptadienols. Crude 1-substituted 2,6-cycloheptadienol prepared from 20 mmol of 2,6-cycloheptadienone was mixed with pulverized boric acid (20 mmol) in a short test tube provided with a glass tube connected to a receiver, and the mixture was heated in an oil bath at 150 °C for five min. The pressure of the system was gradually reduced until the products distilled out and thereafter kept constant. The temperature of the oil bath was then gradually raised to 200 °C. The distillate was extracted with ether, dried, and subjected to distillation. The structure of the 3-substituted tropilidenes was determined by means of NMR; the data are shown in Table 2.

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