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A NEW ROUTE TO ALKYLTROPILIDENES. UNAMBIGUOUS SYNTHESIS OF 3-ALKYL-2,4-DIMETHYLTROPILIDENES

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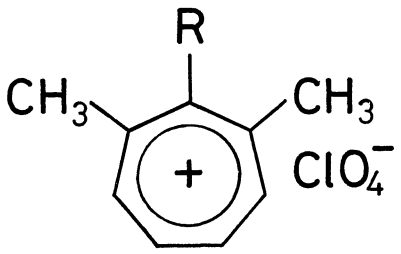
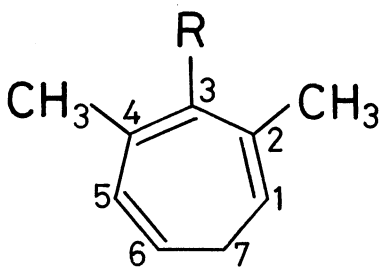
1-Alkyl-2,7-dimethyl-2,6-cycloheptadienols (IV), easily prepared from 2,7-dimethyl-2,6-cycloheptadienone (III) and alkyllithiums, are dehydrated by boric acid to give the corresponding 3-alkyl-2,4-dimethyltropilidenes (II) in good yields. The route provides an unambiguous synthesis of II.

A generally adopted method for the preparation of alkyltropilidenes has been the ring-expansion of the corresponding aromatic hydrocarbons with methylene.[1,2] However, the method usually results in the formation of a mixture of isomers, and moreover, the separation of the products from starting aromatic hydrocarbons encounters difficulties because of the proximity of the boiling points of the starting materials and the products. In the course of our study on one-electron reduction of substituted tropylium ions[3] we required various alkyltropilidenes as the precursors of the corresponding alkyltropylium perchlorates (Ia - Id), and succeeded in exploring a new route to 3-alkyl-2,4-dimethyltropilidenes (IIa - IId).





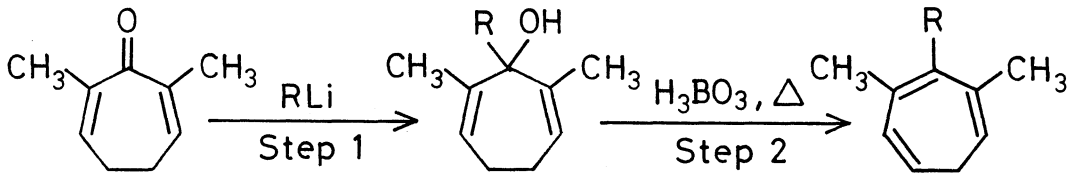
Ia : R = H Ib : R = CH_3
Ic : R = i-Pr Id : R = cyclo-Pr

IIa : R = H IIb : R = CH_3
IIc : R = i-Pr IId : R = cyclo-Pr

The present route involves the addition of alkyllithium to 2,7-dimethyl-2,6-cycloheptadienone (III) and subsequent dehydration of the 1-alkyl-2,7-dimethyl-2,6-cycloheptadienol (IV) accompanied by the migration of a double bond in the presence of boric acid, as shown in the following scheme. In a similar manner, IIa is obtained by using lithium aluminum hydride in place of alkyllithium in the step 1.

The yield in the step 1 was 94, 39, or 85% for R = CH_3, i-Pr, or cyclo-Pr, respectively. The low yield of IVc was found to be due to the concurrent 1,4-addition of isopropyllithium to III. The yields in the step 2 were generally in the range of 70 - 90%. Typical procedures for the steps 1 and 2 are described below for

IId.[4]



III IVb : R = CH_3 II
IVc : R = i-Pr
IVd : R = cyclo-Pr

Treatment of III with cyclopropyllithium in ether afforded IVd in 85% yield. The crude IVd of 90% purity (0.0281 mol), when heated with boric acid (0.033 mol) at 95 Torr with a small flame, afforded a mixture of IId and water as a distillate. Extraction followed by distillation gave IId in 72% yield: bp 71.0 - 75.1°C/3 Torr; NMR (CCl_4, 60 MHz) τ = 4.15 (d, 1, J = 8.0 Hz, C_5-H), 4.57 (dt, 1, J = 8.0, 6.4 Hz, C_6-H), 4.93 (t, 1, J = 6.4 Hz, C_1-H), 7.90 (s, 3, C_4-CH_3), 8.1 (br. s, 3, C_2-CH_3), 8.15 (t, 2, J = 6.4 Hz, C_7-H),[5] 8.5 - 9.7 ppm (multiplets, 5, cyclo-Pr).

The dienone III was prepared as follows. Bromination of 2,7-dimethylcycloheptanone[6] with N-bromosuccinimide in the presence of benzoyl peroxide in refluxing carbon tetrachloride for 25 hr afforded crude 2,7-dibromo-2,7-dimethylcycloheptanone in 95% yield. Subsequent dehydrobromination of the crude dibromide in dimethyl formamide with lithium bromide and lithium carbonate at 110°C under a nitrogen atmosphere gave III in 78% yield: bp 85.8 - 92.5°C/8 Torr; NMR (CCl_4, 60 MHz) τ = 3.63 (m, 2 $>C=C<^{H}$), 7.73 (br. t, 4, $>CH_2$), 8.20 ppm (s, 6, $-CH_3$). Found: C, 79.13; H, 8.92%. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88%.

The present synthetic route is expected to be applicable to the preparation of polyalkyltropilidenes and the research is underway.

References and notes

1) E. Müller, H. Kessler, H. Fricke, and W. Kiedaisch, Justus Liebigs Ann. Chem., 675, 63 (1964).
2) J. Nishimura, J. Furukawa, N. Kawabata, and T. Fujita, Tetrahedron, 26, 2229 (1970).
3) K. Okamoto, K. Komatsu, O. Murai, O. Sakaguchi, and Y. Matsui, Bull. Chem. Soc. Jpn., 46, 1785 (1973), and the references cited therein.
4) Attempts to prepare IId and its isomers by the ring-expansion method[1] failed. Presumably the products are unstable under the reaction conditions.
5) The signal partly overlaps with that of C_2-CH_3.
6) O. S. Bhanot and P. C. Dutta, J. Chem. Soc. (C), 1968, 2589.

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