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Preliminary Communication

Synthesis and Properties of 1,2-Dimethylene-3,5-cycloheptadiene

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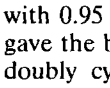
Abstract. The regioselective synthesis of dimethyl 1,3,5-cyloheptatriene-1,2-dicarboxylate (**4**) was achieved by a ring expansion method, starting from dimethyl 1,3-cyclohexadiene-2,3-dicarboxylate (**5**). The title compound **3** was obtained as an air-sensitive oil by zinc-copper reduction of 1,2-bis(bromomethyl)cyclohepta-1,3,5-triene (**10**) to which the diester **4** was transformed.

Dimethylenecycloheptadienes, **1**[1] and **2**[2], had been synthesised and found to be quite expedient as synthetic building blocks for the construction of polycyclic nuclei, depending on their modes of cycloaddition. The title compound **3**[3], one of the isomers of **1** and **2**, had remained unknown despite our earlier effort in which 5,6-bis(bromomethyl)cyclohepta-1,3-diene was subjected to dehydrobromination by a strong base to afford 1,2-homoheptafulvene[4] *via* 1,2-elimination, followed by unexpected 1,3-one instead of consecutive 1,2-one. We wish here to communicate the regioselective synthesis of dimethyl 1,3,5-cycloheptatriene-1,2-dicarboxylate (**4**) and its conversion to the title compound **3**.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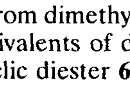
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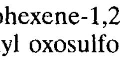
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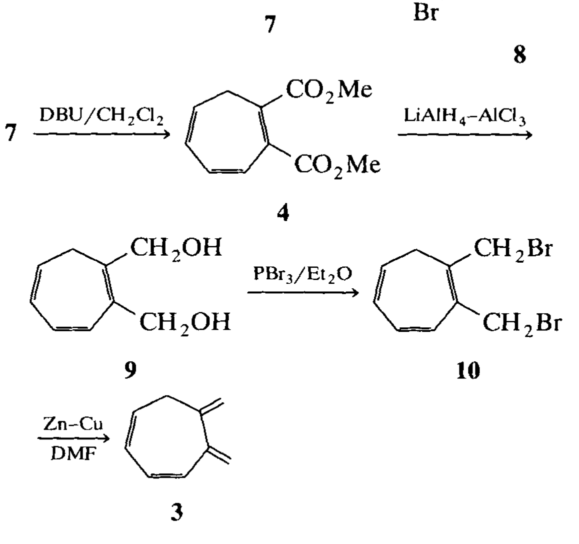
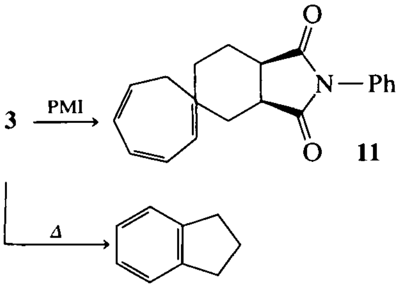
The formation of the diester **4** by thermal rearrangement has been described in the literature[5]. The reported method was not suitable for the present study as it suffered from [1,5] hydrogen shifts which produced regioisomeric diesters concurrently. Thus, by an alternative method, we prepared **4** regioselectively as follows. Cyclopropanation of dimethyl 1,3-cyclohexadiene-2,3-dicarboxylate (**5**), easily prepared from dimethyl cyclohexene-1,2-dicarboxylate[6], with 0.95 equivalents of dimethyl oxosulfonium methylide gave the bicyclic diester **6** in 67% yield, accompanied by a doubly cyclopropanated compound in 3% yield. Allylic bromination of **6** with N-bromosuccinimide (NBS) in CCl_4 afforded a stereoisomeric mixture of the bromides **7** and dimethyl 4-bromocyclohepta-1,3,5-triene-1,2-dicarboxylate (**8**) in 90 and 5% yield, respectively. The bicyclic bromides **7** underwent dehydrobromination by treatment with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in CH_2Cl_2 to give the desired diester **4** as sole product in 92% yield, whose ^1H NMR spectral data were identical with those reported. While reduction of **4** with $LiAlH_4$ gave a mixture of conjugate addition products, in contrast with the case of the isomeric diester, dimethyl 1,3,5-cycloheptatriene-3,4-dicarboxylate[2], a combination of $LiAlH_4$ and $AlCl_3$ reduced only the ester groups of **4**, forming the diol **9**[7] in low yield (33%). The diol **9** was converted to the dibromide **10** by reaction with PBr_3 in ether in 50% yield. The title compound **3** was obtained as a colourless air-sensitive oil in nearly quantitative yield by debromination of **10** with zinc-copper in DMF at room temperature for ca. 15 min. As seen for **1** and **2**, the tetraene **3** in neat liquid also rapidly reacted with atmospheric oxygen to form an interactable oxygen-containing product. A dilute solution of **3** in a hydrocarbon solvent under argon atmosphere was moderately stable, but gradually polymerised on standing



at room temperature for a few days. The reaction of **3** with N-phenylmaleimide (PMI) at room temperature afforded the [4 + 2] cycloadduct **11** in 82% yield. Although a flash thermolysis of the tetraene **3** at 570°C gave a rearranged product, indane[8], in 5% yield, an attempted photochemical isomerisation of **3** in various conditions resulted in gradual decomposition of the starting material without any detection of either the electrocyclised compound, bicyclo[5.2.0]nona-2,3,7(1)-triene[9], or the isomeric tetraene **2** which could be formed by a 1,3-hydrogen shift. Study of the chemical behaviour of **3**, particularly as a synthetic building block, is now in progress.



References and notes

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[5] *N.H. Fischer* and *H.-L. Lin*, J. Org. Chem. **38**, 3073 (1973).

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[7] Physical properties of selected new compounds are as follows. (**3**) ^{1}H NMR (CCl_4): δ ppm 2.89 (d, J = 5.5 Hz, 2H), 4.62 (d, J = 2 Hz, 1H), 4.88 (d, J = 2 Hz, 1H), 5.01 (d, J = 2 Hz, 1H), 5.20 (d, J = 2 Hz, 1H), 5.7–6.2 (m, 4H). IR (CCl_4); νmax 3080w, 3020w, 2940w, 2825m, 1630w, 1430m, 890s cm^{-1}. UV (n-hexane); λmax 246 (log $\epsilon = 3.43$), 253 (3.44), 266^{sh} (3.46), 289 nn (3.61). MS *m/z* 118 (M$^+$, 37%), 117 (100%). (**9**) ^{1}H NMR ($CDCl_3$); δ ppm 2.34 (d, J = 7 Hz, 2H), 3.09 (s, 2H), 4.26 (s, 4H), 5.45 (dt, J = 9, 7 Hz, 1H), 6.13 (dt, J = 9, 3 Hz, 1H), 6.58 (d, J = 3 Hz, 2H). IR (liq. film); νmax 3330brs, 3040m, 2950m, 2870m, 1620w, 1435m, 1140w, 1075m, 990s cm^{-1}. UV (EtOH); λmax 266 nm (log $\epsilon = 3.51$). MS *m/z* 152 (M$^+$, 7%), 91 (100%). (**10**) colourless prisms, mp 41–43°C. ^{1}H NMR ($CDCl_3$); δ ppm 2.40 (d, J = 7 Hz, 2H), 4.11 (s, 2H), 4.13 (s, 2H), 5.55 (dt, J = 9, 7 Hz, 1H), 6.16 (ddd, J = 9, 4.5, 2 Hz, 1H), 6.55 (m, 2H). IR (KBr); νmax 3040m, 2960m, 2880w, 2840w, 1605w, 1460m, 1440m, 1370w, 1315w, 1255w, 1200s cm^{-1}. UV (EtOH); λmax 214^{sh} (log $\epsilon = 4.12$), 234^{sh} (4.07), 279 nm (3.77). MS *m/z* 280, 278, 276 (M$^+$, 3, 7, 4%), 117 (100%). (**11**) ^{1}H NMR ($CDCl_3$); δ ppm 2.10 (dd, J = 12, 6.5 Hz, 1H), 2.4–3.0 (m, 5H), 3.24 (m, 2H), 5.33 (dt, J = 9, 6.5 Hz, 1H), 6.04 (dm, J = 9 Hz, 1H), 6.45 (m, 2H), 7.01 (m, 2H), 7.32 (m, 3H). IR (liq. film); νmax 3020w, 2950m, 1775w, 1710vs, 1600w, 1500s, 1450w, 1430m, 1385s, 1315m, 1150s, 1055m, 1005w cm^{-1}. UV (EtOH); λmax 261 (log $\epsilon = 3.45$), 265^{sh} (3.45), 269^{sh} nm (3.44). MS *m/z* 291 (M$^+$, 83%), 130 (100%).

[8] Since 8-phenylbicyclo[5.2.0]nona-1,3,5-triene was reported to rearrange to 2-phenylindane on heating, **3** presumedly undergoes thermal electrocyclisation of the dimethylene moiety and subsequent 1,5-hydrogen shifts to form bicyclo[5.2.0]nona-1,3,5-triene, which then rearranges to indane; *E.E. Waali* and *W.M. Jones*, J. Am. Chem. Soc. **95**, 8114 (1973).

[9] A mixture of bicyclo[5.2.0]nonatrienes had been synthesised by cyclopropanation of cyclobutabenzene; *R.P. Thummel* and *P. Chayankoon*, J. Org. Chem. **48**, 596 (1983).