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SYNTHESIS OF ENDO-MONOMETHYLENE ADDUCTS OF 7-SUBSTITUTED NORBORNENES AND NORBORNADIENES

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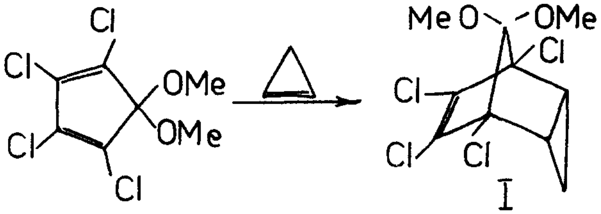
The reaction of cyclopropene with cyclopentadiene to give the adduct (V)[1,2] could conceivably be extended and so provide a synthetic method for the preparation of endomonomethylene adducts of 7-substituted norbornenes and norbornadienes. The recent report[1] of a simple synthesis of cyclopropene makes this synthetic route extremely convenient. The present communication presents the results of our investigations along these lines.

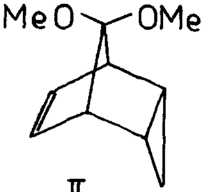
Reaction of cyclopropene with 1,1-dimethoxy-2,3,4,5-tetrachlorocyclopentadiene[3] in isopentane at 0°C gave the crystalline adduct (I) (m.p. 69.5-70.0)[4] in 60% yield based on the substituted cyclopentadiene. The p.m.r. spectrum of (I) showed signals (τ-scale, relative to T.M.S.) at 6.37 (singlet; relative area: 2.95), 6.49 (singlet; rel. area 2.95) and a well resolved ABX_2 pattern with centres of gravity of the signals occurring at 8.2 (rel. area 1.83), 9.1 (ref. area 1.20) and 9.6 (rel. area 1.03)[5]. The configuration of the cyclopropane ring was shown to be endo by conversion of (I) to the tricyclic hydrocarbon (IV) in the following manner.

Dechlorination of (I) according to the procedure of Winstein[6] could be controlled[7] to give pure (III) or a mixture of the unsaturated ketal (II) and the saturated ketal (III). Substitution of sodium for lithium in this reaction[8] gave pure (II). The unsaturated ketal (II) displayed p.m.r. signals at τ4.38 (triplet; rel. area 1.99), 6.84 (singlet; rel. area 3.05), 6.89 (singlet; rel. area 3.05), 7.25 (pentuplet; rel. area 1.91), 8.5 to 8.9 (multiplet; rel. area 2.09) and 9.2 to 9.7 (multiplet; rel. area 2.04). In the infrared spectrum the unsaturated ketal (II) gave characteristic absorption at 3055 cm^{-1} (cyclopropane C-H stretch)[12], 3040 cm^{-1} (olefinic C-H stretch)[13], 1040 cm^{-1} (cyclopropane ring deformation)[13] and 662, 682, 712 cm^{-1} (cis-1,2-α-substituted olefinic deformation)[13].

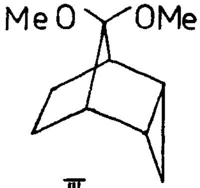
The saturated ketal (III) gave p.m.r. signals at τ6.76 (singlet; rel. area 2.90), 6.85 (singlet; rel. area 2.90), 7.97 (pentuplet; rel. area 2.02) and 8.1 to 9.5 (unresolved



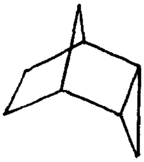
I



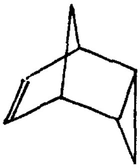
II



III



IV



V

multiplet; rel. area 8.20). Characteristic infrared absorption occurred at 3065, 3025, 3020 and 1032 cm^{-1}.

Acid hydrolysis of the saturated ketal (III) with 3N aqueous perchloric acid in tetrahydrofuran gave the corresponding ketone (I.R. absorption at 1825, 1780 and 1766 cm^{-1}) which was reacted with p-toluenesulphonyl hydrazide[9] to yield the tosylhydrazone. Subsequent reduction[10] of the tosylhydrazone with sodium borohydride in dioxane gave the hydrocarbon (IV). This product proved to be identical (V.P.C. retention time and infrared) to the tricyclic hydrocarbon resulting from catalytic reduction of the tricyclic olefin (V) obtained according to the method of Closs[1].

Our initial attempts to hydrolyse the unsaturated ketal (II) proved to be most interesting for they resulted in quantitative yields of tropilidene. This facile decarbonylation reaction is not to be unexpected and may be compared with other attempts to prepare substituted 7-norbornadienones which defy isolation as such and result in quantitative yields of substituted benzenes[14]. However in the present instance, careful hydrolysis of the unsaturated ketal (II) did give the corresponding ketone as a crystalline solid which on warming to room temperature decarbonylated to tropilidene. In cyclohexane solution at 30°C this ketone had a half life of approximately 10 minutes. The infrared spectrum of the ketone showed absorption typical of bridged carbonyl compounds[11] at 1860, 1820 and 1780 cm^{-1} as well as absorption at 3065 and 3045 (cyclopropane C-H stretch)[12], 3015 cm^{-1} (olefinic C-H stretch), 1040 cm^{-1} (cyclopropane ring deformation) and 692 cm^{-1} (*cis*-1,2-disubstituted olefinic deformation)[13]. The p.m.r. spectrum showed signals at τ 3.92 (triplet; rel. area 1.90), 6.83 (multiplet; rel. area 1.98), 8.2 to 8.8 (multiplet; rel. area 2.00), 9.0 to 9.5 (multiplet; rel. area 1.14) and 9.7 to 10.0 (multiplet; rel. area 0.99).

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