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TRANSANNULAR CYCLIZATION OF CYCLOOCTA-1,5-DIENE INDUCED BY THALLIUM(III) TRIFLUOROACETATE

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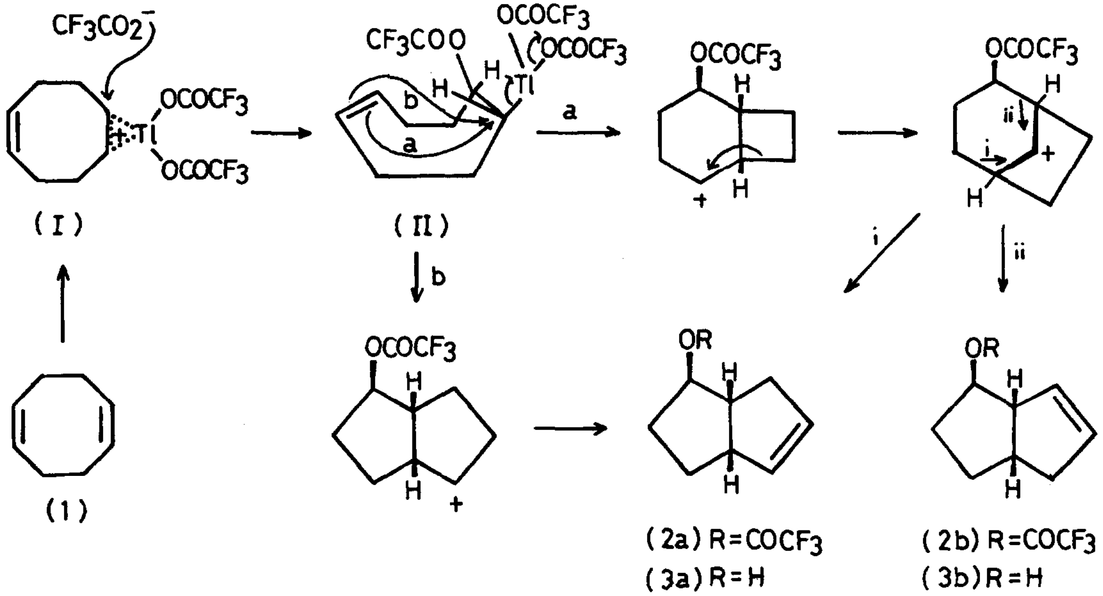
Although extensive studies on the reaction of thallium(III) salts[1)] have been reported in recent years, reports on the reaction of polyolefins with thallium(III) salts were limited[2,3)]. Previously we have found that an acyclic 1,5-diene underwent an olefinic cyclization[4)] leading to predominantly five-membered carbocyclic products upon treating it with thallium(III) perchlorate. Now we wish to describe a transannular cyclization of a cyclic diene, cycloocta-1,5-diene (1) induced by thallium(III) trifluoroacetate affording bicyclo-[3.3.0]octenol derivatives (2a) and (2b). As compared with the reaction of (1) with mercury(II) acetate[5)] giving also the bicyclo[3.3.0]octane ring system, the present reaction is remarkably characterized by the difference in the reaction path way.

Reaction of (1)(5.0 g) with thallium(III) trifluoroacetate(25.1 g, 1.0 equiv.) in dried CH_2Cl_2(2000 ml) at room temperature for 16 hr gave colourless liquid [b.p. 43-46°/2 mm, IR($CHCl_3$) 1775 cm^{-1}, ^1H NMR($CDCl_3$) δ 5.53(m, olefinic H) ppm, Mass m/e 220(M^+), 52 % yield]. Although the substance showed a single peak on gas chromatography under the various conditions, this is obviously a mixture of the trifluoroacetates (2a) and (2b) with a ratio of 3:2 on the basis of the following evidences : i) the ^{19}F NMR(CCl_4) signal of the trifluoromethyl group(+13.0 ppm from that of trifluoromethylbenzene as an internal reference) split into two peaks (the ratio of the intensities, 3:2) when the signal was extremely expanded; ii) the ^{13}C NMR spectrum of the substance showed sixteen signals due to the skeletal carbons corresponding to (2a) and (2b). Alkaline hydrolysis of the mixture of (2a) and (2b) afforded the corresponding alcohols (3a) and (3b), which were hydrogenated over Pd-C yielding exo-cis-bicyclo-[3.3.0]octan-2-ol[6)] as a sole product. On oxidation of the mixture of (3a) and (3b) with CrO_3-pyridine followed by reduction with $NaBH_4$, endo-cis-bicyclo-[3.3.0]oct-6-en-2-ol[5)] and endo-cis-bicyclo[3.3.0]oct-7-en-2-ol[7)] were isolated after separation by preparative gas chromatography (15 % PEG 20M).

Both compounds (2a) and (2b) with the same exo configuration are presumably formed by the reaction path way as illustrated.



In the case of the reaction of (1) with mercury(II) acetate in the presence of perchloric acid, Julia and Colomer[5)] reported that the direct transannular attack of the remaining double bond to the π complex initially formed, corresponding to (I), resulted an epimeric mixture of exo and endo acetates of (3a). In the present reaction, the oxythallation of (1) via the π complex (I) to (II) occurs apparently prior to the transannular cyclization.

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