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A NOVEL ACID-CATALYZED REARRANGEMENT OF CYCLOBUTANOLS[a]

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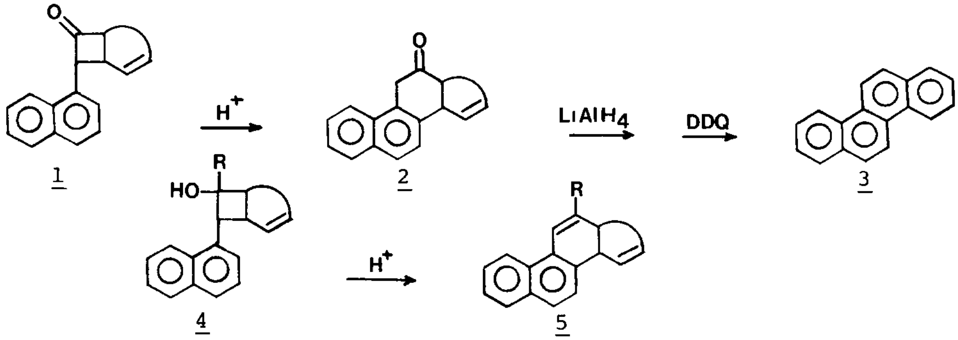
ABSTRACT: Under acid-catalysis 7-arylbicyclo[3.2.0]hept-2-en-6-ols rearrange to diarylmethanes and cyclopenteno-annelated polycyclic aromatic hydrocarbons.

In our continuing efforts to develop novel synthetic methods for ring annelations we have investigated the possibility of using α-aryl substituted bicyclic cyclobutanols and cyclobutanones as synthetic intermediates towards the preparation of polycyclic aromatic hydrocarbons (PAH's) and steroids. Cyclobutanones such as 1 rearrange under acidic conditions to give β-tetralones 2 which can be converted to PAH's such as 3 by simple chemical elaboration.[1-3] We have recently shown that cyclobutanols such as 4 will



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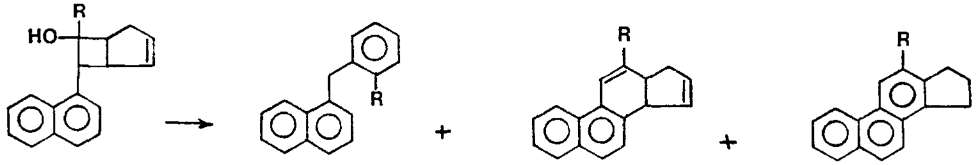
[a] Part VII in a series of acid-catalyzed rearrangements of cyclobutanones
For Part VI see ref 1.

undergo similar reaction to yield substituted hydroaromatic derivatives 5[4] which serve as potential precursors to arene epoxides. In the present communication we wish to report on a novel rearrangement of 7-aryl substituted bicyclo[3.2.0]hept-2-en-6-ols under acidic conditions. Alcohols 6-11[5] were prepared from the corresponding cyclobutanones by reduction with $LiAlH_4$ or methylation with $LiCH_3$. In all cases one stereoisomer was obtained as evident from nmr spectroscopy. The aryl group in the 7-monoarylcyclobutanols 6-9 was assigned the endo stereochemistry based on the benzilic-bridgehead hydrogens coupling constant of 8 Hz in the pmr spectrum. This assignment is consistent with that for the aryl group in the starting cyclobutanones.[3] The hydroxyl group has been assigned the endo configuration based on the α-H benzilic-H coupling constant (J = 7 Hz) as well as the slow exchange of the hydroxyl hydrogen (doublet, J = 10 Hz) indicating possible hydrogen bonding to the aryl group in the secondary alcohols 6, 8 and 10. The preparation of 11 from $LiAlH_4$ reduction of bicyclo[3.2.0]hept-2-en-6-one has been reported[11] to give an 80:20 mixture of endo and exo alcohols respectively.

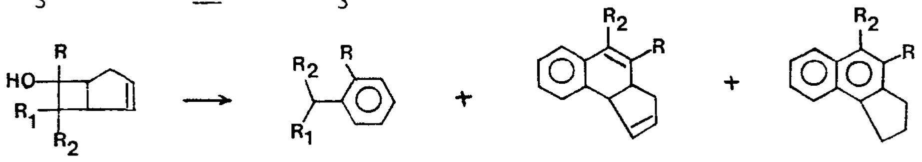


6 R = H
7 R = CH_3

12 R = H
13 R = CH_3

17 R = H

18 R = H



8 R_1=C_6H_5, R_2=R=H
9 R_1=C_6H_5, R_2=H, R=CH_3
10 R_1=R_2=C_6H_5, R=H
11 R_1=R_2=R=H

14 R_1=C_6H_5, R_2=R=H
15 R_1=C_6H_5, R_2=H, R=CH_3
16 R_1=R_2=C_6H_5, R=H

19 R_2=R=H
20 R_2=C_6H_5,R=H

21 R_2=R=H
22 R_2=C_6H_5, R=H

These alcohols 6-10 were transformed under acidic conditions (methanesulfonic acid at room temperature or phosphorus pentoxide under reflux benzene) to produce diarylmethanes 12-16 as a major product as well as ring annelated derivatives 17-22. Yields of these products are summarized in Table 1. The identity of compounds 12, 14, 15, 16, 18, and 21 were established by comparison with authentic samples or spectral data reported in the literature for the same compounds.[6-8] The structure of 13 was assigned based on spectral data as well as its similarity in the pmr spectrum to that of 15. Structures 17, 19 and 20 were assigned on the basis of their conversions to the benzoindans 18, 21 and 22 respectively with acid.

Table 1. Yields of Products from Rearrangement of Bicycloheptanols

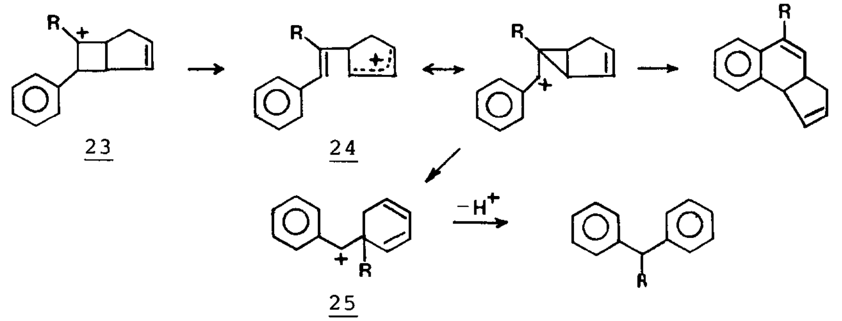
Bicycloheptenol	Method	Diarylmethanes	Ring-annelated products
6	P_2O_5/C_6H_6	12 (60%)[a]	17 (20%) 18 (5%)
7	CH_3SO_3H	13 (65%)[a]	unidentified (25%)
8	P_2O_5/C_6H_6	14 (55%)[b]	19 (30%) 21 (5%)
9	CH_3SO_3H	15 (70%)[b]	unidentified
10	CH_3SO_3H	16 (30%)[a]	20 (30%) 22 (10%)

a. isolated yields by preparative thin layer chromatography (silica gel, 10% benzene in hexane eluant)

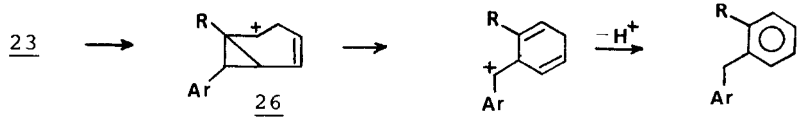
b. isolated yields by preparative gas chromatography (6 ft,10% carbowax, 210° C)

The formation of ring-annelated products can be rationalized according to scheme A. A similar mechanism has been proposed for the rearrangement

Scheme A



Scheme B



of cyclobutanones such as 1.[3] The production of diarylmethanes can be accounted for by invoking the same ion 24 undergoing a thermally allowed 1,5 hydrogen shift to produce a (1,3-cyclohexadien-5-yl)-methyl cation 25 which is followed by 1,2 hydride shift and deprotonation. Alternatively endo bond cleavage of ion 23 leads to a norcar-4-en-2-yl cation 26 followed by cyclopropyl ring opening, 1,2 hydride shift and deprotonation as in Scheme B. On the basis of the product distribution in the methyl derivatives 7 and 9 it would appear that mechanism A does not play an important part in the formation of diarylmethanes. The parent norcar-4-en-2-yl ion (similar to 26) is known to rearrange to give mainly products derived from cyclohepta-1,3-dien-5-ylium.[9] The parent bicyclohept-2-en-6-ol (11) (70% endo, 30% exo[11]) under our experimental conditions did not give 1,3,5-cycloheptatriene but resulted only in endo to exo isomerization of the starting alcohol. However under more vigorous conditions (500°C, Al_2O_3) alcohol 11 has been reported to be transformed quantitatively to 1,3,5-cycloheptatriene.[10] In our studies no cycloheptatrienes were observed from alcohols 6-10. This is in accord with the 7-aryl group promoting the exocyclopropyl bond cleavage in ion 26 leading to a more stable species. We are planning to investigate the nature of some of these carbocation intermediates by nmr studies under stable ion conditions.

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