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ON THE BASE CATALYZED CYCLIZATION OF 2-ALKYL-2-p-TOLUENESULFONOXYMETHYLCYCLOHEXANONES

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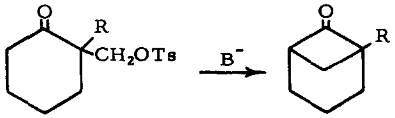
The reaction of 2-alkyl-2-p-toluenesulfonoxymethylcyclohexanones with base has been found by three groups to give bicyclo[3.1.1]heptane derivatives.[1] In investigating this reaction with a variety of bases, we



have found that the product is a mixture of two ketones, formed in about equal amount. They may be separated by preparative vapor phase chromatography, and were found to be isomeric. Both have an infrared band at 5.64μ, characteristic of cyclobutanones. The n.m.r. spectra did not give much information, except that when R = CH_3, the methyl peak was a sharp singlet indicating the absence of protons on the adjacent carbon.

One of the ketones (A) was found to give no exchange with deuterium oxide and base, whereas the other (B) had three exchangeable hydrogens. The data then suggest the structures:

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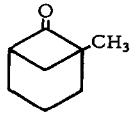
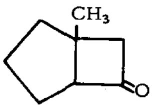
[1] W.H. Brown, Ph.D. Thesis, Columbia University, 1958; E. Wenkert and D.P. Strike, J. Org. Chem. 27, 1883 (1962); F. Nerdel, D. Frank and H. Marschall, Angew. Chem. Int. Ed. 1, 457 (1962).



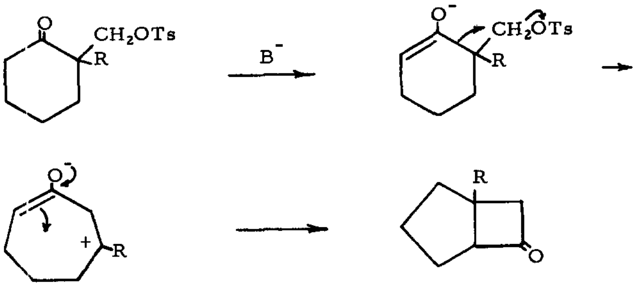
A



B

The structure of B was demonstrated by nitric acid oxidation to a dicarboxylic acid which readily formed an anhydride. The melting point of the acid agreed with that of cis-1-methylcyclopentane-1, 2-dicarboxylic acid[2] and the structure of the anhydride was confirmed by the presence of infrared bands at 5.42 and 5.63μ, characteristic of a five membered ring anhydride, and by the presence of an unsplit methyl peak at 8.46τ in the n.m.r. spectrum.

The transformation of the tosylate to B is interesting. It does not proceed in the absence of base, and thus probably involves the anion of the starting ketone. The process may then be visualized as a neopentyl type rearrangement with the oxyvinyl group acting as the migrating group.



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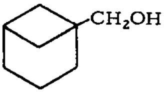
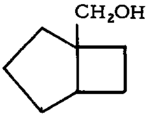
[2] Reported m.p. 128-129° (W. E. Bachmann and E. R. Strove, J. Am. Chem. Soc. 63, 1262 (1941); and m.p. 124-126° (P. C. Dutta, J. Indian Chem. Soc. 17, 611 (1940); found m.p. 123-125°. cis-1-Methylcyclopentane-1, 3-dicarboxylic acid had m.p. 96-97° (S. Beckmann and R. Schaber, Ann. 585, 154 (1954).

The reactions provide a useful route to bridgehead substituted compounds of types A and B. With R = $CH_2OCH_2C_6H_5$, the ring closure followed by a Wolff-Kishner reduction and hydrogenolysis gives C and D which are of particular interest in our study of bicyclic small ring compounds.[3]



C



D

We wish to thank the Army Research Office, Durham, for its support of this investigation.

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[3] Cf. K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Am. Chem. Soc.* **83**, 3998 (1961).