

Bridge Fission in the Bicyclo[4,2,1]nonan-9-one Series

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Reaction of ethyl *endo*- and *exo*-7-tosyloxy-9-oxobicyclo[4,2,1]nonane-1-carboxylates and of ethyl 9-oxobicyclo[4,2,1]non-7-ene-1-carboxylate with ethanolic sodium ethoxide leads by bridge fission to diethyl cyclo-octene-1,4-dicarboxylate.

We have previously reported¹ the conversion of the *endo*- and *exo*-tosylates (I) into the bicyclo[4,2,1]nonenone (II) and the isomeric non-6(7)-enone by reaction with boiling collidine. We now find that with sodium ethoxide in ethanol the reaction takes a different course, affording diethyl cyclo-octene-1,4-dicarboxylate (III) by fission of the carbonyl bridge. Similar bridge-fission reactions have been noted before.² The structure of the product follows from its elemental composition and from spectroscopic data. The u.v. spectrum (λ_{max} 223 nm; ϵ 10,530) shows the presence of an $\alpha\beta$ -unsaturated ester group,³ and this is supported by the i.r. absorption, ν_{max} 1705 and 1732 (CO₂Et) and 760 cm⁻¹

(>C=CH-). In the n.m.r. spectrum signals due to the two ester groups are readily distinguished and the presence of a single olefinic proton is indicated by a signal centred at τ 3.05 (β -proton in an $\alpha\beta$ -unsaturated carbonyl compound⁴). Catalytic hydrogenation readily afforded a dihydro-compound in which the ester groups are equivalent.

The ring-opened product (III) could reasonably arise from the tosylate (I) by a retro-Claisen reaction followed by β -elimination (Scheme 1) or, alternatively, by initial elimination to give the enone (II) followed by retro-Claisen ring opening with migration of the double

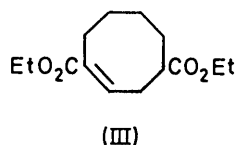
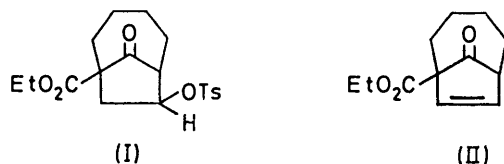
¹ W. Carruthers and M. I. Qureshi, *J. Chem. Soc. (C)*, 1970, 2238.

² See G. L. Buchanan, *Topics Carbocyclic Chem.*, 1969, 1, 227.

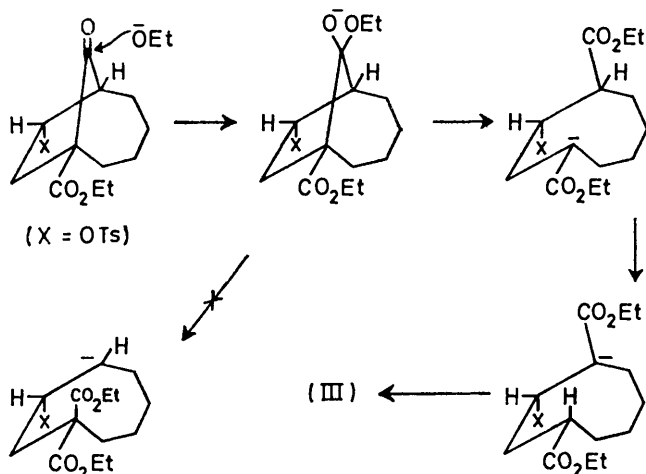
³ Cf. A. I. Scott, 'Interpretation of the Ultraviolet Spectra of Natural Products,' Pergamon, London, 1964, p. 80.

⁴ D. H. Williams and I. Fleming, 'Spectroscopic Methods in Organic Chemistry,' McGraw-Hill, London, 1966, p. 128.

bond. Precedents for both schemes are known.⁵ Support for the latter possibility is provided by the ready

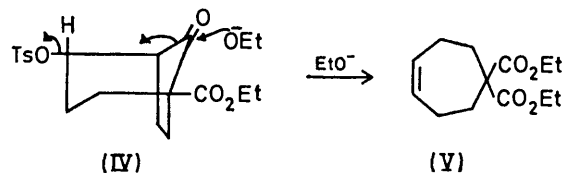


conversion of (II) into (III) when treated with ethanolic sodium ethoxide under the same conditions as tosylate (I).*



SCHEME 1

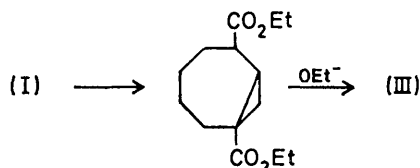
Another type of ring-opened product is exemplified by the *gem*-dicarboxylic ester (V), obtained by reaction



SCHEME 2

of ethanolic sodium ethoxide with the equatorial

* A referee suggests the following alternative pathway:



tosylate (IV)⁶ (Scheme 2). No comparable product was obtained in the present case, presumably because the tosyloxy-group in the rigid five-membered ring cannot easily adopt the necessary conformation to allow concerted fragmentation to take place.

EXPERIMENTAL

U.v. spectra were measured with a Unicam SP 800 spectrophotometer and refer to solutions in 95% ethanol. I.r. spectra were measured with a Perkin-Elmer Infracord. Mass spectra were recorded with a Hitachi RMU 60 instrument. ¹H N.m.r. spectra were determined with a Perkin-Elmer 60 MHz instrument, for solutions in carbon tetrachloride or deuteriochloroform, with tetramethylsilane as internal reference.

Thin (0.25 mm) and thick (1.0 mm) layer chromatography plates were prepared from Kieselgel (Merck).

Reaction of Ethyl 9-Oxo-7-endo-p-tolylsulphonyloxybicyclo[4,2,1]nonane-1-carboxylate with Sodium Ethoxide.—The tosylate (130 mg) was added to a solution of sodium ethoxide in ethanol [from sodium (8.7 mg) and ethanol (4 ml)]. The solution was heated under reflux for 20 h, cooled, diluted with water, and extracted with ether. The recovered neutral material (78 mg) showed only one major spot on t.l.c. (solvent ether). Preparative layer chromatography and distillation gave *diethyl cyclo-octene-1,4-dicarboxylate* (68 mg) as an oil, b.p. 110° at 0.1 mmHg (air-bath temp.) [Found: C, 66.2; H, 9.0%; *M* (mass spectrum) 254. C₁₄H₂₂O₄ requires C, 66.1; H, 8.7%; *M*, 254; λ_{max}, 223 nm (ε 10,530); ν_{max} (film) 1732s, 1705s, 1648m, and 760m cm⁻¹, τ 3.10 (1H, m), 5.85 (q, *J* 7.0 Hz, CO₂·CH₂·CH₃), 5.81 (q, *J* 7.0 Hz, CO₂·CH₂·CH₃), 7.43 (5H), and 8.47 (6H).

A solution of this material (100 mg) in ethanol (10 ml) was hydrogenated at room temperature and pressure over palladised charcoal (10%; 50 mg), affording *diethyl cyclo-octane-1,4-dicarboxylate* (94 mg) as an oil, b.p. 95° at 0.1 mmHg (air-bath temp.) (Found: C, 65.6; H, 9.5. C₁₄H₂₄O₄ requires C, 65.6; H, 9.4%); ν_{max} (film) 1732 cm⁻¹; τ 5.81 (4H, q, *J* 7.8 Hz), 8.76 (6H, t, *J* 7.8 Hz), and 7.5 (2H, m); *m/e* 211 (*M* - OEt) (no molecular ion).

The acidic product of the fission reaction (20 mg) showed one major spot on t.l.c. Esterification with diazoethane, preparative layer chromatography, and distillation afforded *diethyl cyclo-octene-1,4-dicarboxylate* (14 mg).

Similar results were obtained when the *exo*-tosylate (I) and ethyl 9-oxobicyclo[4,2,1]non-7-ene-1-carboxylate (II) were treated with sodium ethoxide in ethanol under the same conditions.

We thank the Dawood Foundation, Pakistan, and the University of Exeter, for financial support (to M. I. Q.).

[2/1828 Received, 2nd August, 1972]

⁵ G. L. Buchanan and G. W. McLay, *Tetrahedron*, 1966, **22**, 1521; G. L. Buchanan, A. McKillop, and R. A. Raphael, *J. Chem. Soc.*, 1965, 833; A. C. Cope, E. S. Graham, and D. J. Marshall, *J. Amer. Chem. Soc.*, 1954, **76**, 6159.

⁶ G. L. Buchanan and G. W. McLay, *Tetrahedron*, 1966, **22**, 1521.