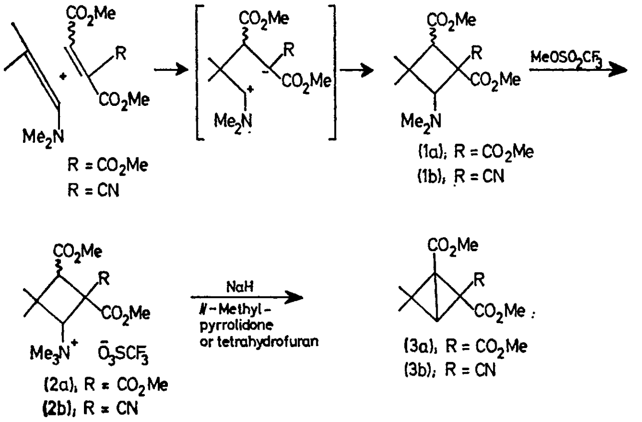
Electronegatively Substituted Bicyclobutanes *via* the Cycloaddition of Trisubstituted Electron-Poor Olefins to Enamines

By HENRY K. HALL, JUN.* and PIERRE YKMAN

(*Department of Chemistry, University of Arizona, Tucson, Arizona,* 85721)

Summary Cycloaddition of trisubstituted electron-poor olefins such as trimethylethylenetricarboxylate to enamines such as *N,N*-dimethylisobutenylamine, quaternization, and base-induced elimination lead to electronegatively substituted bicyclobutanes such as trimethyl 4,4-dimethylbicyclobutane-1,2,2-tricarboxylate.

BRANNOCK,[1] Stork,[2] and other workers have described the cycloaddition of *N,N*-dimethylisobutenylamine (and other enamines) to methyl acrylate (and other monosubstituted electron-poor olefins). Charge stabilization in the zwitterion intermediate causes the electron-poor group and the dimethylamino group to occur in the 1,2-positions in the cycloadduct. Quaternization and base elimination lead to the cyclobutene.



We have now used trisubstituted electron-poor olefins in the enamine cycloaddition reaction to give a new synthesis of certain bicyclobutane derivatives. Because the carbanion portion of the zwitterion is more effectively stabilized by two electronegative groups than by one, the lone electronegative group and the dimethylamino group are now found in the 1,3-positions in the cycloadducts (**1**). Thus, (**1a**) is formed in almost quantitative yield in ether solution, m.p. 44—51°.[†] Quaternization with methyl trifluoromethanesulphonate in dichloromethane solution at −70° gave (**2a**), m.p. 143·5—145°, (84%). With NaH in *N*-methylpyrrolidone or tetrahydrofuran, this salt, 10 g, yielded trimethyl 4,4-dimethylbicyclobutane-1,2,2-tricarboxylate (**3a**), m.p. 44—46°, 1·0—1·3 g, (20—30%).[‡]

Similarly, dimethyl cyanoethylene-1,2-dicarboxylate added smoothly to *N*,*N*-dimethylisobutenylamine to give cycloadduct (**1b**), m.p. 78—82°, (78%). Quaternization with methyl trifluoromethanesulphonate gave salt (**2b**), m.p. 170—171°C, (65%); sodium hydride in *N*-methylpyrrolidone gave bicyclobutane (**3b**), m.p. 49·5—52°, (20%).

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[†] All new compounds gave C and H analyses within ± 0·3% of the calculated values; their i.r., n.m.r., and m.s. data also agreed with the assigned structures.

[‡] Variations caused by solvent change, by-products in these reactions, and variants of this synthesis are being investigated by Dr. J. Otton.

[1] K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelly, *J. Org. Chem.*, 1964, **29**, 801.
[2] G. Stork, H. Brizzolara, H. Landesman, J. Smuszkovicz, and R. Terrel, *J. Amer. Chem. Soc.*, 1963, **85**, 207.