Chemical Conversions using Sheet Silicates: Ready Dimerization of Diphenylethylene

By John M. Adams, Samuel H. Graham, Paul I. Reid and John M. Thomas*
(*Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth* SY23 1NE)

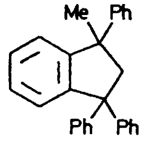
Summary Cation-exchanged montmorillonites function as efficient catalysts for the production of 1-methyl-1,3,3-triphenylindan from 1,1-diphenylethylene at low temperature.

Recent chemical interest in the phenomenon of intercalation has been focussed largely on preparative and electronic aspects of various intercalates formed principally by transition metal chalcogenides[1] and by graphite.[2] Less attention has been paid to the role of intercalates as means of accomplishing novel stereo- and regio-specific reactions. It is clear, however, on the basis of what is already known[3,4] of the interlamellar compounds formed between sheet-silicates and various organic molecular species that considerable scope exists for the development of a range of novel reactions which proceed with little thermal activation when cation-exchanged montmorillonites are employed.

When the interlamellar ions of natural clays are replaced by transition-metal cations, especially by Cu^{II}, powerful catalysts for dimerization and oligomerization are generated. Thus *trans*-stilbene is smoothly converted into a dimer, in very good yield, and indene yields oligomeric products with no loss of hydrogen.[3] Both *trans*-stilbene and indene were introduced separately from the vapour into dehydrated Cu^{II}–montmorillonite (see ref. 3 for further details).

Here we report the ready production of the derivative (II) from the parent (I) when the latter was heated to reflux for 30 min in contact with Cu^{II}-exchanged montmorillonite (cation exchange capacity 66 mequiv./100 g) which had not been especially dried. The Na^+-exchanged clay also serves as a catalyst but is less efficient than the Cu^{II}-exchanged analogue. The dimer, which crystallized from the cooled reaction mixture, was obtained (*ca.* 30%) as prisms, m.p. 142 °C (lit. 142—143 °C), from acetic acid, and was identical with that reported by Schoepfle and Ryan[5] and by Bergman and Weiss[6] and shown by them to be 1-methyl-1,3,3-triphenylindan (II). The ^1H n.m.r. spectrum was consistent with this structure; the diastereotopic methylene protons gave rise to an AB quartet, δ_A 3·1, δ_B 3·41 p.p.m., and J_{AB} 14 Hz. These chemical shifts are larger than might have been anticipated for non-benzylic protons. This new procedure seems to provide the most convenient preparation of this dimer.

$Ph_2C=CH_2$
(I)



(II)

Though the mechanism of this and many other reactions of ion-exchanged sheet silicates await full elucidation, in this instance at least the general effect is that of a Lewis acid type catalyst. We know, however, that interlamellar Cu^{II} may, in general, activate olefinic bonds or anchor unsaturated molecules *via* linkages with these bonds. Further reactions, to be reported fully elsewhere, bear out this generalization.

We thank the S.R.C. for financial support.

(*Received*, 11*th November* 1976; *Com.* 1245.)

---

[1] A. D. Yoffe, *Chem. Soc. Rev.*, 1976, 51; M. B. Dines, *Science*, 1975, **188**, 1210; B. Bach and J. M. Thomas, *J.C.S. Chem. Comm.*, 1972, 301; W. B. Davies, M. L. H. Green, and A. J. Jacobsen, *ibid.*, 1976, 781; C. Riekel and R. Schöllhorn, *Material. Res. Bull.*, 1975, **10**, 629; M. S. Whittingham and F. R. Gamble, *ibid.*, p. 363.

[2] A. R. Ubbelohde, *Proc. Roy. Soc.*, 1972, **A327**, 289; J. G. Hooley, *Carbon*, 1972, **10**, 155; E. L. Evans and J. M. Thomas, *J. Solid State Chem.*, 1975, **14**, 99; L. B. Ebert, *Ann. Rev. Materials Sci.*, 1976, **6**, 181.

[3] J. M. Thomas, J. M. Adams, S. H. Graham, and (in part) D. T. B. Tennakoon, paper presented at Centennial Meeting, American Chemical Society, New York, April, 1976; D. T. B. Tennakoon, Ph.D. Thesis, University of Wales (Aberystwyth), 1974; M. J. Tricker, D. T. B. Tennakoon, J. M. Thomas, and S. H. Graham, *Nature*, 1975, **253**, 110.

[4] B. K. G. Theng, 'The Chemistry of Clay-Organic Reactions,' Adam Hilger, London, 1974; D. B. Fenn, M. M. Mortland, and T. J. Pinnavaia, *Clays and Clay Minerals*, 1973, **21**, 315; A. Weiss, in 'Organic Geochemistry,' eds. G. Eglington and M. J. T. Murphy, Springer-Verlag, Berlin, 1969.

[5] C. S. Schoepfle and J. D. Ryan, *J. Amer. Chem. Soc.*, 1930, **52**, 4021.

[6] E. Bergman and H. Weiss, *Annalen*, 1930, **480**, 49.