

The Free-radical Addition of Thiols to *cis,cis*-Cyclo-octa-1,5-diene

By J. M. LOCKE and E. W. DUCK

(Research and Development Laboratories, International Synthetic Rubber Co. Ltd., Southampton)

FREE-RADICAL reactions of *cis,cis*-cyclo-octa-1,5-diene (I) have recently been investigated by three groups¹⁻³ who all concluded that the free-radical additions resulted in a transannular 1,5-cyclo-addition to give derivatives of bicyclo[3,3,0]octane. The generality of the reaction was demonstrated by a range of reactants.¹⁻³

We have shown that if equimolar amounts of *cis,cis*-cyclo-octa-1,5-diene and a thiol or thiol-acid are mixed at room temperature an excellent yield of the simple adduct is obtained which arises from the addition of the thiol to one of the double bonds.

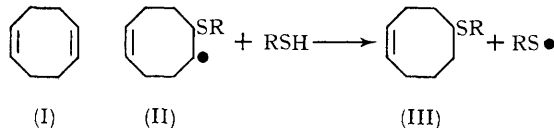
In particular the reaction between thiolacetic acid and *cis,cis*-cyclo-octa-1,5-diene at room temperature results, by a strongly exothermic reaction, in an 84% yield of the simple adduct (III; R = Ac), b.p. 80—83°/0.25 mm., n_D^{25} 1.5160—1.5181; λ_{\max} . (in cyclohexane) 233 m μ (ϵ 3,700); ν_{\max} . 3000 (=CH—) and 1675 cm.⁻¹ (thiolester). The n.m.r. spectrum of (III) showed a multiplet centred at τ 4.35 (two coincident triplets) which can be assigned to the olefinic protons.*

A similar reaction with thiolbenzoic acid gave the adduct (III; R = Bz) in 65% yield, b.p. 140—150°/0.09 mm., n_D^{25} 1.5800—1.5827; λ_{\max} . (in cyclohexane) 238 (ϵ 11,450), 244, and 270 m μ (ϵ 7,200); ν_{\max} . 3000 (=CH—) 1645 cm.⁻¹ (thiolester). The n.m.r. spectrum showed a multiplet at τ 4.31. Hydrolysis of (III; R = Ac or Bz) with methanolic potassium hydroxide gave the

corresponding thiol (ν_{\max} . 3000 cm.⁻¹) whose n.m.r. spectrum showed a multiplet at τ 4.36. The thiol formed a 2,4-dinitrophenyl sulphide derivative, m.p. 105—106°. Gas chromatography of (III; R = Ac) (at 170°) and (III; R = Bz) (at 200°) on a 2 ft. column of 8% butanediol succinate on HMDS Chromosorb W† showed only one component in each case.

The generality of this reaction was shown by the addition of benzenethiol to *cis,cis*-cyclo-octa-1,5-diene in 69% yield. The i.r. and n.m.r. spectra were again in agreement with the suggested structure (III; R = Ph) (ν_{\max} . 3000 cm.⁻¹, τ 4.34). Gas chromatography again showed only one component.

A possible reason for the anomalous reaction of thiols with *cis,cis*-cyclo-octa-1,5-diene is their great tendency to act as chain-transfer agents; the step II \rightarrow III would then be much faster than in the corresponding radical-initiated addition of the addends, used by Dowbenko² and by Friedman.³



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* A sample of cyclo-oct-4-en-1-ol prepared according to A. C. Cope and P. E. Peterson, *J. Amer. Chem. Soc.*, 1959, **81**, 1643, had an n.m.r. spectrum with a multiplet (overlapping triplets) at τ 4.32.

† The resolving power of the column was such that a mixture of *cis,trans,trans*-, and *trans,trans,trans*-cyclododeca-1,5,9-trienes could be separated at 140°.

¹ G. Pregaglia and G. Gregorio, *Chimica e Industria*, 1963, **45**, 1065.

² R. Dowbenko, *Tetrahedron*, 1964, **20**, 1843.

³ L. Friedman, *J. Amer. Chem. Soc.*, 1964, **86**, 1885.