Chemical Communications

(The Journal of The Chemical Society, Section D)

NUMBER 8/1970 22 APRIL

1,2,5,6-Tetramethylenecyclo-octane

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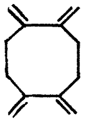
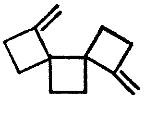
Summary A convenient two-step synthesis of 1,2,5,6-tetramethylenecyclo-octane from 1,2-dimethylenecyclobutane is described.

A reaction of great synthetic utility in the formation of polycyclic carbon skeletons is transannular photochemical ring closure,[1] and a molecule whose structure is likely to be suitable for such a process is 1,2,5,6-tetramethylenecyclo-octane (**1**).[2] We report a convenient two-step synthesis of this compound.

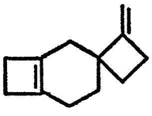


(1)

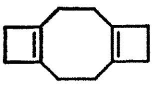
Yields of 1,2-dimethylenecyclobutane (**2**) using literature procedure[3] for the dimerization of allene could be greatly improved by recycling the pyrolysate. On benzophenone-sensitized photodimerization[4] of (**2**) in degassed benzene solution, three major products were obtained which were readily separable by g.l.c. on a 10 ft. × $\frac{3}{8}$ in. column of 20% SE-30 on Chromasorb-W. They were characterized by their mass spectra as dimers of (**2**) and identified, in order of elution (peak area ratios **4** : **1** : **2**) as (**3**), (**4**) and (**5**) by 100 MHz n.m.r.



(3)



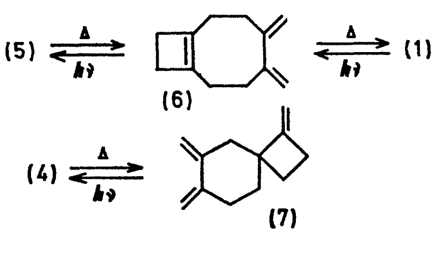
(4)



(5)

The spectrum of (**3**) showed a slightly split singlet at δ 4·83 (4H), a multiplet extending from 2·3—2·6 (4H), and a broad multiplet between 1·6 and 2·3 (8H). Compound (**4**) had a highly split multiplet centred at δ 4·75 (2H), a multiplet centred around 2·6 (4H), a slightly split singlet at 2·47 (2H), a very broad singlet centred at 2·05 (4H), and a multiplet around 1·75 (4H). The n.m.r. of (**5**) had two singlets of equal area at δ 2·27 and 2·15.

That (**5**) is not a primary photoproduct could be deduced from inspection of the n.m.r. spectrum of the crude photolysate. No peaks corresponding to (**5**) were present, but several absorptions not present in either (**3**) or (**4**) were observed. On refluxing the benzene solution, over the course of several hours these absorptions disappeared as those corresponding to (**5**) increased in intensity. By analogy with the formation of 1,5-cyclo-octadiene by Cope rearrangement of *cis*-1,2-divinylcyclobutane,[5] the precursor of (**5**) is almost certainly the *syn*-isomer of (**3**). Its geometry, unlike that of (**3**), disposes it favourably for a concerted Cope rearrangement, which relieves the strain present in the system of three spiro-fused rings.



On pyrolysis in a flow system at 330° with a contact time of 3 sec., (**5**) gave exclusively (**1**) [$m/e = 160$; correct elemental analysis; n.m.r. ($CDCl_3$) δ 4·90 (d, 4H, J 2 Hz), 4·80 (d, 4H, J 2 Hz), 2·40 (s, 8H); u.v. λ_{max} (hexane) 228 nm, log ϵ 4·0]. At 270° (**6**), identified by u.v. and n.m.r., could also be isolated. Direct photolysis of (**1**) in hexane with a low-pressure mercury lamp also produced (**6**)

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which, on continued photolysis, finally regenerated (**5**). The direct photolysis of (**1**) in addition gives rise to a product of transannular photo-ring closure.[6]

When pyrolysed at 330°, (**4**) produced (**7**) and (**3**) gave an equal mixture of (**1**) and (**7**). Compound (**7**) was identified by its n.m.r. and u.v. spectra and by its conversion back into (**4**) on direct photolysis.

The synthesis of (**1**) outlined above is especially convenient because it can be carried out in high yield without isolation of any of the intermediates. Thus, the crude mixture[3] of allene dimers, after a simple distillation to remove higher oligomers, can be used in the sensitized photodimerization; and the crude photolysate can be pyrolysed at 330° to give, in 85% overall yield from (**2**), a 3:2 mixture of (**1**) and (**7**). Although we had hoped that pyrolysis of the crude photolysate at higher temperatures would allow the isolation of pure (**1**), this did not prove to be so. Starting with either pure (**1**) or (**7**), a 1 : 1 equilibrium mixture of the two was obtained on pyrolysis at 500°. Nevertheless, (**1**) and (**7**) can be readily separated on a preparative scale with an 8 ft. × $\frac{3}{8}$ in. column of 20% Carbowax 20 M on Chromasorb-W. Moreover, in direct photolysis of (**1**), no complications are caused by the presence of (**7**) or its photoproduct, (**4**).

(*Received, February 9th,* 1970; *Com.* 187.)

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[1] See, for instance, the two syntheses of cubane: P. E. Eaton and T. W. Cole, jun., *J. Amer. Chem. Soc.*, 1964, **86**, 3157, and J. C. Barborak, L. Watts, and R. Pettit, *ibid.*, 1966, **88**, 1329.

[2] The 1,3,5,7-isomer has been obtained from the catalysed tetramerization of allene and undergoes a transannular cycloaddition reaction with tetracyanoethylene, J. K. Williams and R. E. Benson, *J. Amer. Chem. Soc.*, 1962, **84**, 1257.

[3] A. T. Bloomquist and J. A. Verdol, *J. Amer. Chem. Soc.*, 1959, **78**, 109.

[4] Review: N. J. Turro, "Molecular Photochemistry," Benjamin, New York, 1965, pp. 212—216.

[5] G. S. Hammond and C. D. DeBoer, *J. Amer. Chem. Soc.*, 1964, **86**, 899, and references therein.

[6] W. T. Borden, I. L. Reich, L. Sharpe, and H. J. Reich, *J. Amer. Chem. Soc.*, submitted for publication.