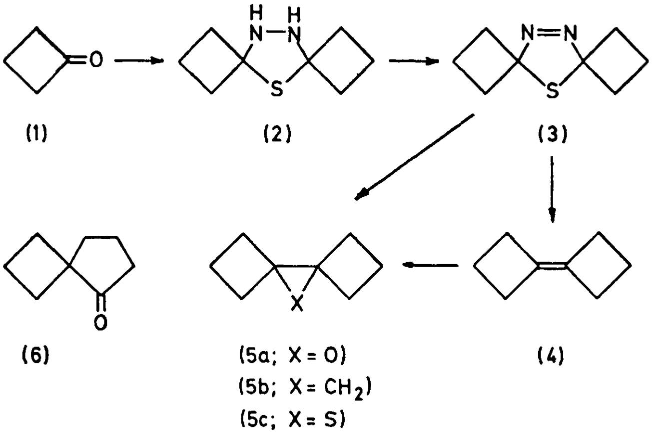
Bicyclobutylidene

By John W. Everett and P. J. Garratt*

(*Chemistry Department, University College London, 20 Gordon Street, London* WC1H OAJ)

Summary Bicyclobutylidene has been synthesised in a three-step synthesis from cyclobutanone; reaction of bicyclobutylidene with methylene gave dispiro[3,0,3,1]-nonane, and reaction with *m*-chloroperoxybenzoic acid gave 9-oxadispiro[3,0,3,1]nonane.

Bicyclobutylidene (**4**) is one of the few remaining simple ethylene derivatives which had not been prepared, probably owing to the ease of rearrangement of the cyclobutane ring, which precludes a number of obvious synthetic routes to (**4**). We now report a three-step synthesis of (**4**) in high yield, using the recently described method of Barton[1] and Kellogg[2] and their respective co-workers.



(1) (2) (3)

(6) (4)

(5a; X = O)
(5b; X = CH_2)
(5c; X = S)

Reaction of cyclobutanone (**1**) with hydrazine and H_2S at −20°[3] led to the thiadiazolidine (**2**) (82%), m.p. 96—97°,† which on oxidation with lead tetra-acetate at 0° yielded the thiadiazoline (**3**) (92%), m.p. 72—73°.† Reaction of (**3**) with Ph_3P at 85° for 1 h[1] gave the desired bicyclobutylidene (**4**) (92%), b.p. 85° at 100 mmHg as a colourless liquid.† The n.m.r. spectrum (CCl_4) was completely consistent with the assigned structure, showing signals at τ 7·34—7·64 (8H, t, allylic) and 7·88—8·28 (4H, m, CH_2).

Reaction of (**4**) with *m*-chloroperoxybenzoic acid in Et_2O at 0° gave 9-oxadispiro[3,0,3,1]nonane (**5a**) (57%) as a colourless liquid.† Treatment of (**4**) with CH_2I_2/Zn–Cu couple[4] yielded the liquid dispiro[3,0,3,1]nonane (**5b**) (35%)† [τ 7·79—8·27 (12H, m, cyclobutane) and 9·72 (s, 2H, cyclopropane)]. 9-Thiadispiro[3,0,3,1]nonane (**5c**), m.p. 36—37°, was prepared (98%) by pyrolysis of (**3**) at 85° under N_2 for 20 min.[1,2]

The dispiro-compounds (**5a**)—(**5c**) exhibit a range of thermal stability. Thus, (**5a**) at 150° was smoothly converted into the known spiro[4,3]octan-1-one (**6**) (68%),[5] (**5c**) decomposed at this temperature to a number of products, while (**5b**) was stable up to 250°.

We thank Eli Lilly International Corporation for generous financial support.

(*Received, 7th April* 1972; *Com.* 591.)

---

† Analytical and spectral data for all new compounds were in accord with the assigned structures.

[1] D. H. R. Barton, E. H. Smith, and B. J. Willis, *Chem. Comm.*, 1970, 1226; D. H. R. Barton and B. J. Willis, *J.C.S. Perkin I*, 1972, 305.

[2] R. M. Kellogg and S. Wassenaar, *Tetrahedron Letters*, 1970, 1987.

[3] K. Rühlmann, *J. prakt. Chem.*, 1959, **8**, 285.

[4] See E. LeGoff, *J. Org. Chem.*, 1964, **29**, 2048.

[5] E. Vogel, *Chem. Ber.*, 1952, **85**, 25.