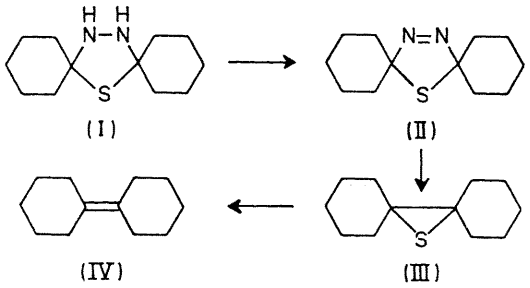
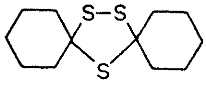
Olefin Synthesis by Twofold Extrusion Processes. Some Further Examples

By D. H. R. BARTON,* E. H. SMITH, and B. J. WILLIS
(*Imperial College, London, S.W.7*)

Summary Further examples of olefin synthesis by twofold extrusion processes are given.

IN the preceding communication[1] we outlined a new approach to olefin synthesis which should be particularly applicable to highly hindered olefins. We describe now further illustrative examples.





(V)

Treatment of cyclohexanone with hydrazine and hydrogen sulphide affords[2] in quantitative yield the tetrahydrothiadiazole (I). The latter was oxidized by lead tetraacetate in light petroleum (b.p. 60—80°) at 0° to the azo-sulphide (II) (95%), m.p. 80—81°, ν_{max} (KBr) 1575 cm^{-1}, λ_{max} (EtOH) 286 and 325 nm (ϵ 330 and 225, respectively). On heating the azo-sulphide (II) at 100° for 1 hr. in the presence of triphenylphosphine (1·1 moles) bis-cyclohexylidene (IV) (77%), nitrogen, and triphenylphosphine sulphide were formed. The reaction sequence has the thiiran (III) as intermediate. Interestingly,[1,3] photolysis of the azo-sulphide in cyclohexane (medium-pressure mercury arc lamp) gave cyclohexanone azine (52%), but no olefin (IV).

While our manuscript was in preparation the formation of the azo-sulphide (II) from the hydrazine (I) was also reported.[4] It was shown that pyrolysis gave the thiiran (III) and that photolysis afforded cyclohexanone azine.

Oxidation of the azo-sulphide (II) with hydrogen peroxide in acetic acid gave the corresponding azo-sulphoxide (96%), m.p. 146—147° decomp., ν_{max} (Nujol) 1570 and 1040 cm^{-1}. Further oxidation of this azo-sulphoxide with peracetic acid in dichloromethane gave the corresponding azo-sulphone (98%), m.p. also 146—147°, ν_{max} (Nujol) 1310 and 1130 cm^{-1}, λ_{max} (cyclohexane) 366 nm (ϵ 140). Pyrolysis of the sulphoxide or the sulphone gave only poor yields of bis-cyclohexylidene (IV). Photolysis of the sulphoxide or the sulphone in cyclohexane again afforded cyclohexanone azine (54 and 18%, respectively), but no olefin (IV).

In principle one might expect the trithia-system, as in the readily available[5] (V), to be susceptible to the twofold extrusion process. However, in agreement with previous observations,[6] the compound (V) resists attack by many tervalent phosphorus reagents [triethyl phosphite, triphenylphosphine, tris(diethylamino)phosphine], and with tributylphosphine it is slowly desulphurised, but no bis-cyclohexylidene (IV) is formed.

We thank Dr. D. G. Hewitt for his participation in the initial stages of this work.

(*Received, July 1st*, 1970; *Com.* 1055.)

---

[1] D. H. R. Barton and B. J. Willis, preceding communication.
[2] K. Rühlmann, *J. prakt. Chem.*, 1959, **8**, 285.
[3] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, 1970.
[4] R. M. Kellogg and S. Wassenaar, *Tetrahedron Letters*, 1970, 1987.
[5] F. Asinger, M. Thiel, G. Lipfert, R. E. Plessmann, and J. Mennig, *Angew. Chem.*, 1958, **70**, 372; F. Asinger and M. Thiel, *ibid.*, p. 667; F. Asinger, M. Thiel, and G. Lipfert, *Annalen*, 1959, **627**, 195.
[6] D. S. Breslow and H. Skolnik, "Multi-sulfur and Sulfur and Oxygen Five- and Six-membered Heterocycles," Interscience, New York, 1966, p. 70.