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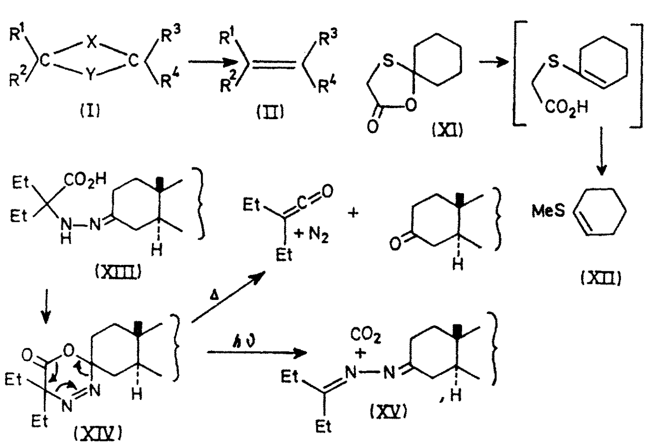
Olefin Synthesis by Twofold Extrusion Processes

By D. H. R. Barton* and B. J. Willis
(*Imperial College, London, S.W.7*)

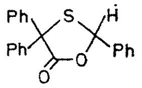
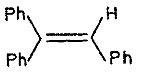
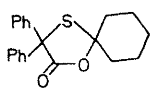
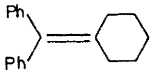
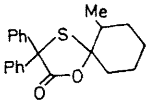
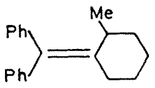
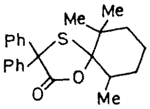
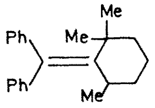
Summary A new principle of olefin synthesis is adumbrated, which should be particularly applicable for highly hindered olefins.

Although there are many known olefin-forming reactions, of which the Wittig reaction is of special significance, there is still need for a general reaction which will afford even highly hindered olefins in good yield using readily available reagents. In principle, the twofold extrusion process [(I) → (II)], where R¹ *etc.* are alkyl, aralkyl, aryl *etc.* and X and Y are easily extrudable fragments, would enable highly hindered olefins to be synthesized. This is because the olefin bonds would both be formed intramolecularly, whilst the nature of X and Y can be chosen to avoid problems of steric compression. We illustrate this principle with a simple example. Other examples will be recorded later.



The condensation of thiobenzilic acid,¹ $Ph_2C(SH)CO_2H$ with benzaldehyde and with various ketones under acid catalysis gave the oxathiolan-5-ones (III), (IV), (V), and (VI) (see Table), in general, in high yield. The best results were obtained using toluene-*p*-sulphonic acid (azeotropic removal of water) or boron trifluoride gas in benzene. Heating these various oxathiolan-5-ones in the presence of tris(diethylamino)phosphine gave good yields of the corresponding olefins (VII), (VIII), (IX), and (X), respectively. The formation of the highly hindered olefin (X) is noteworthy.

Table

Oxathiolan-5-one		Olefin formed	
	(III) 150–160°, 2 hr		(VII) (95%)
	(IV) 160–200°, 5 hr		(VIII) (82%)
	(V) 200–240°, 6 hr		(IX) (81%)
	(VI) 180–230°, 4 hr		(X) (80%)

Compounds (V) and (VI) were mixtures of two isomers, which were not separated.

Earlier work² on the pyrolysis of the compound (III) and related benzaldehyde derivatives showed that loss of carbon dioxide gave the corresponding thiirans, which afforded olefins (and sulphur) in relatively low yield.

Although this synthesis of olefins affords highly hindered compounds with ease, it is not applicable unless phenyl or other conjugating residues are present to facilitate (radical) loss of carbon dioxide. Thus similar pyrolysis of the oxathiolan-5-one (XI) with triphenylphosphine at 220° gave only the methylthioether (XII).

An apparently attractive olefin synthesis would result if X were (–N=N–) and Y were (–CO–O–) in formula (I). We report the first synthesis of such a system and a study of its pyrolysis and photolysis. Condensation of cholestanone with α-ethyl-α-hydrazinobutyric acid[3] in ethanol gave the hydrazone (XIII) (76%). Oxidation of the latter with lead tetra-acetate in dichloromethane at $-18°$ afforded the azo-lactone (XIV) (65%), m.p. 95—96° decomp., $[\alpha]_D + 14°$ (in tetrahydrofuran), λ_{max} (tetrahydrofuran) 368 nm (ϵ 130), ν_{max} ($CHCl_3$) 1740 and 1590 cm^{-1}. Pyrolysis of the azo-lactone (XIV) at 115° gave, smoothly, diethylketen (identified by trapping with ethanol and with cyclohexylamine and by its i.r. spectrum), cholestanone, and nitrogen. There was no trace of the expected olefin. In marked contrast, photolysis of the azo-lactone (XIV) in cyclohexane (medium-pressure mercury arc lamp), gave the mixed azine (XV) and carbon dioxide. It is clear that the difference in the pyrolysis and photolysis reactions of the azo-lactone has interesting theoretical implications.[4]

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[1] H. Becker and A. Bistrzycki, *Ber.*, 1914, **47**, 3149.
[2] C. T. Pedersen, *Acta Chem. Scand.*, 1968, **22**, 247.
[3] A. Carmi, G. Pollak, and H. Yellin, *J. Org. Chem.*, 1960, **25**, 44.
[4] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, 1970.