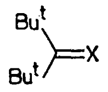
Synthesis and Properties of Monomeric Selenoketones

By Thomas G. Back, Derek H. R. Barton,* Michael R. Britten-Kelly, and Frank S. Guziec, Jr.
(*Chemistry Department, Imperial College, London* SW7 2AY)

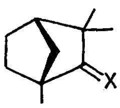
Summary The preparation and reactions of di-t-butyl selenoketone (Ib) and of (−)-selenofenchone (IIb) are described; fenchylidenefenchane (VI) has been synthesised.

To our knowledge saturated monomeric selenoketones have never been described. We report the preparation and properties of this unusual class of compound.

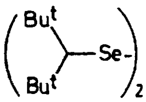
Heating di-t-butyl ketone triphenylphosphoranylidene hydrazone[1] (Ia), m.p. 109—110° (1 equiv.) with selenium powder (2 equiv.) and a trace of tri-n-butylamine under nitrogen at 120 °C for 20 h gave on distillation the blue di-t-butyl selenoketone (Ib) (30—35%), b.p. 83—85 °C at 30 mmHg, λ_{max} (cyclohexane) 230, 268, and 710 nm (ϵ 2800, 7200, and 21 respectively), δ (CCl_4) 1·53 (s).

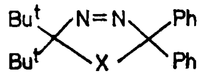

(I)

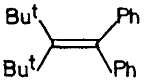
a; X = N-N=PPh_3
b; X = Se
c; X = S
d; X = SO
e; X = O

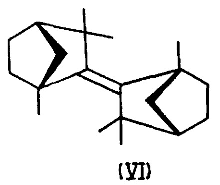

(II)

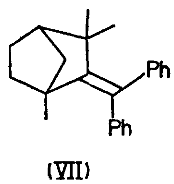
a; X = N-N=PPh_3
b; X = Se
c; X = S


(III)


(IV) a; X = Se
b; X = S


(V)


(VI)


(VII)

Similarly, the (−)-fenchone derivative[1] (IIa), m.p. 142—145 °C, gave, on heating at 160 °C with continuous removal of volatile material at 5 mmHg, (−)-selenofenchone (IIb) (28%) as blue crystals, m.p. (from ether at −30 °C) 41—47 °C, λ_{max} (cyclohexane) 224, 272, and 616 nm (ϵ 3700, 9600, and 42 respectively). Both selenoketones are stable under nitrogen on prolonged heating at 150 °C.

Oxidation of di-t-butyl thioketone[2] (Ic) with *m*-chloroperbenzoic acid in ether gave di-t-butyl sulphine (Id) (> 90%), m.p. 43—45 °C, λ_{max} (EtOH) 264 nm (ϵ, 9000), a very stable compound. In contrast, similar oxidation of the selone (Ib), gave, even at 0 °C, only di-t-butyl ketone (Ie) and red selenium.

The selone (Ib) was immediately reduced by sodium borohydride to give, on aerobic work up, the diselenide (III). If the phosphine derivative (Ia) is not completely free from the parent hydrazone this same diselenide (and congeners) is formed at the expense of the selone (Ib).

Diphenyldiazomethane reacted immediately at 0 °C with the selone (Ib) to furnish 5,5-diphenyl-2,2-di-t-butyl-Δ^3-1,3,5-selenadiazoline (IVa) (73%), m.p. (from light petroleum at 0 °C) 114—118 °C (decomp.). On heating in CCl_4 this gave the known[2] olefin (V) (67%) and selenium. A competition expt. with Ph_2CN_2 (1 mol.), thioketone (Ic), (1 mol.), and (Ib) (1 mol.) showed immediate formation of (IVa), but no formation of (IVb).[2] The selenoketone is, therefore, much more reactive towards diazo-compounds.

The (−)-fenchone derivative (IIa) (1 equiv.) was heated with selenium (2 equiv.) and a trace of tri-n-butylamine at 160 °C under nitrogen for 24 h without distillation. Extraction of the residue gave the olefin (VI) (24%), m.p. (from light petroleum) 125—127 °C, $[\alpha]_D$ − 240°. This suggested that the selone (IIb) had reacted with the derivative (IIa) in the manner already adumbrated.[2] In agreement, heating (−)-thiofenchone (IIc) with the derivative (IIa) at 160 °C for 45 h gave the olefin [as (VI)] (72%) as a mixture of isomers, m.p. 110—115 °C. The pure isomer (VI) is tentatively assigned the *trans* configuration. It is the most hindered olefin yet prepared.

We note that 2-diphenylmethylenefenchane[2] (VII) has the following constants: (−), m.p. 156—157·5 °C, $[\alpha]_D$ −360·2°, (±)-[previously reported[2] as (+)], m.p. 140—141·5 °C, $[\alpha]_D$ 0°, (+), m.p. 153—157 ° C, $[\alpha]_D$ + 367·2°.

All new compounds gave correct analytical data and, where not quoted, the appropriate physical constants. All $[\alpha]_D$ are in EtOH.

(*Received, 25th April* 1975; *Com.* 479.)

[1] Prepared by the method of H. J. Bestmann, and H. Fritzsche, *Chem. Ber.*, 1961, **94**, 2477.
[2] D. H. R. Barton, F. S. Guziec, Jr., and I. Shahak, *J.C.S. Perkin I*, 1974, 1794.