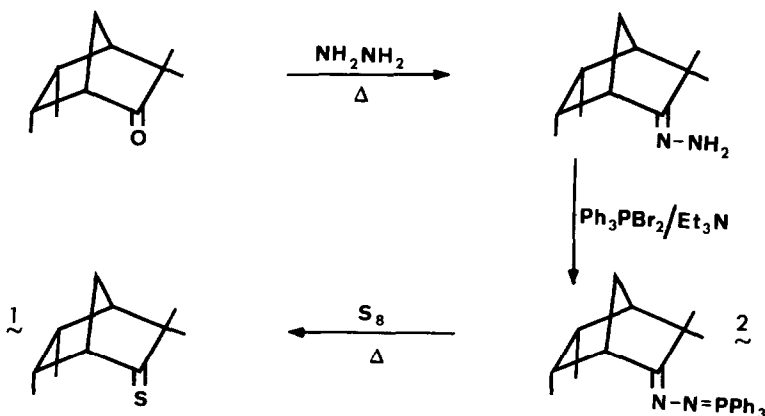


## A SYNTHESIS OF HIGHLY HINDERED THIOKETONES

Paul de Mayo, Gražina L. R. Petrašiūnas and Alan C. Weedon

*Department of Chemistry, The University of Western Ontario, London, Canada, N6A 5B7*

Many methods for the preparation of thioketones have been reported<sup>1</sup> but few possess the advantage of wide applicability. The more general or most commonly used procedures available, viz. treatment of the corresponding ketone with anhydrous hydrogen chloride and hydrogen sulphide<sup>1</sup>, with boron sulphide<sup>2</sup>, or with phosphorus pentasulphide<sup>1</sup>, involve acidic reaction conditions and in the latter two cases application of heat. We required the sterically hindered thioketone 1 for photochemical studies<sup>3</sup>, but found that the corresponding ketone was sensitive to the conditions of these standard methods of thioketone preparation, yielding only decomposition products presumably derived from acid-catalysed rearrangement. We report here a method particularly suitable for the synthesis of 1 and other hindered thioketones from the corresponding ketones which avoids these problems.



The procedure involves thermal decomposition of the readily prepared triphenylphosphorane hydrazone of the ketone (e.g. 2) in the presence of elemental sulphur; an analogue of

the method of Barton *et al* for the preparation of selenoketones<sup>4</sup>. Typically, the triphenylphosphorylidene hydrazone (1.5 mmol) and sulphur (ca 50 mmol) were melted together under vacuum (1-5 mm Hg) at 130 - 140°C, and the thioketone was continuously distilled out into a cold trap. The results for a number of representative hindered thioketones are given in the table; the yields shown are not optimized values. In the cases of di-*tertiary*-butyl thioketone and 2,2,5,5-tetramethylcyclopentane thioketone, the reaction was also successfully carried out under nitrogen at atmospheric pressure and the thioketone was distilled out under reduced pressure at the end of the reaction. The thioketone 1 codistilled with polar impurities which were easily removed by filtration through silica gel in pentane<sup>5</sup>, whilst the other thioketones distilled out free of contamination. If too low a pressure was used in the preparation of di-*tertiary*-butyl thioketone (ie < 5mm), the product contained traces of di-*tertiary*-butyl diazomethane.

T A B L E

Thione	Isolated Yield %
<u>1</u> <sup>5</sup>	13
2,2,5,5-tetramethylcyclopentane thione <sup>12</sup>	41
thiofenchone	42
di- <i>tertiary</i> -butyl thione	83

Di-*tertiary*-butyl thioketone has been prepared previously by an indirect route<sup>6</sup> but its synthesis by application of more standard procedures to the ketone has not been reported whilst 2,2,5,5-tetramethylcyclopentane thioketone has been synthesized in our laboratory from the corresponding ketone using boron sulphide or anhydrous hydrogen chloride and hydrogen sulphide, but in inferior yield<sup>3</sup>. Thiofenchone has previously been prepared from the ketone with anhydrous hydrogen chloride and hydrogen sulphide in 9% yield<sup>7</sup>.

The reaction failed for the preparation of thiocamphor, thiobenzophenone and thioacetophenone. When the triphenylphosphorylidene hydrazone of benzophenone<sup>8</sup> was heated with

sulphur the isolated products were triphenylphosphine sulphide (76%) and tetraphenylethylene (90%). We note that this contrasts with the reported<sup>9</sup> products of thermal decomposition of the same compound in benzene (where diphenyldiazomethane and carbene derived species were obtained) which may suggest that thiobenzophenone is an intermediate but reacts rapidly with the starting material or other reaction intermediates to give the olefin. Barton *et al*<sup>6</sup> also observed olefin formation when either selenium or hindered thioketones were heated with the triphenylphosphorylidene hydrazone of benzophenone. Presumably the thioketones shown in the table are isolable because analogous reaction is inhibited by steric effects.

Heating the triphenylphosphorylidene hydrazones of camphor<sup>6</sup> and acetophenone<sup>8</sup> with sulphur resulted in vigorous decomposition and the production of apparently polymeric material, perhaps because of the possibility of thioenolization of these thioketones and their further reaction.

#### Acknowledgement

The authors wish to thank the National Research Council of Canada for Financial Support.

#### References

1. See, for instance, D. Paquer, *Int. J. Sulphur Chem. (B)*, 7, 269 (1972).
2. F.M. Dean, J. Goodchild and A.W. Hill, *J. Chem. Soc. (C)*, 2192 (1969).
3. D.S.L. Blackwell, K.H. Lee, P. de Mayo, G.L.R. Petrašiūnas and G. Reverdy, Manuscript in preparation.
4. T.G. Back, D.H.R. Barton, M.R. Britten-Kelly and F.S. Guziec, *J.C.S. Perkin I*, 2079 (1976). See also H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 2, 635 (1919).
5. Following chromatography, 1 was further purified by cooling methanol or pentane solutions to give a glassy solid, mp 78 - 85°C; <sup>1</sup>H-NMR (100 MHz, CDCl<sub>3</sub>) δ 3.28 (m, 1H), 2.60 - 2.35 (m, 2H), 2.28 (m, 1H), 2.05 (m, 1H), 1.63 (m, 1H), 1.26 (s, 3H), 1.20 (s, 3H), 1.07 (d, 3H, J = 7Hz), 0.83 (d, 3H, J = 7Hz); m/e 182 (M<sup>+</sup>, 46%), 167 (12), 126 (59), 125 (58),

111 (89), 94 (100); precise mass, found 182.1127 (calc. for  $C_{11}H_{18}S$ , 182.1129); U.V./-VIS. (pentane) 244nm ( $\epsilon = 12,000$ ), 491nm ( $\epsilon = 11.4$ ). The ketone precursor of **1** was prepared by 2-step dimethylation of 5 *endo*, 6 *endo* - dimethylbicyclo(2.2.1) - heptan-2-one<sup>12</sup> using sodium amide in ether and methyl iodide<sup>13</sup> in 40% yield as a colourless oil, I.R.  $1748\text{ cm}^{-1}$  (film); m/e 166 (M<sup>+</sup>, 18%), 151 (2), 137 (2.5), 135 (2), 123 (18), 112 (17), 97 (100), 85 (82), 52 (56), precise mass, found 166.1359 (calc. for  $C_{11}H_{18}O$ , 166.1358). The hydrazone was prepared by the method of Barton<sup>4</sup> in 60% yield and was unstable with respect to azine formation on standing. The hydrazone had mp  $81-2^\circ$  (pentane), I.R.  $3360, 3220\text{ cm}^{-1}$  (Nujol); m/e 180 (M<sup>+</sup>, 34%), 165 (21), 124 (80), 123 (100); precise mass, found 180.1623 (calc. for  $C_{11}H_{20}N_2$ , 180.1626). The triphenylphosphorylidene hydrazone was prepared by the method of Bestmann *et al*<sup>8</sup>, and used directly.

6. D.H.R. Barton, F.S. Guziec and I. Shahak, J.C.S. Perkin I, 1794 (1974).
7. D.C. Sen, J. Indian Chem. Soc., 12, 647 (1935); *ibid.* 14, 214 (1937).
8. H.J. Bestmann and H. Fritzsche, Chem. Ber., 94, 2477 (1961); H.J. Bestmann and L. Gothlich, Ann. Chem., 655, 1 (1962).
9. D.R. Dalton, and S.A. Liebmann, Tetrahedron, 25, 3321 (1969).
10. G. Singh and H. Zimmer, J. Org. Chem., 30, 417 (1965).
11. 2,2,5,5-tetramethylcyclopentanone hydrazone was prepared from the ketone by the method of Barton<sup>4</sup> in 84% yield and had mp  $66.5 - 67.5^\circ\text{C}$  (pentane); I.R.  $3400, 3220\text{ cm}^{-1}$  (Nujol); precise mass, found 154.1468 (calc. for  $C_9H_{18}N_2$ , 154.1470). The triphenylphosphorylidene hydrazone was prepared by the method of Bestmann *et al*<sup>8</sup> in 66% yield and had mp  $119.5 - 121^\circ\text{C}$  (isopropanol); precise mass found, found 414.2225 (calc. for  $C_{27}H_{31}N_2P$ , 414.2225).
12. H.N. Miller and K.W. Greenlee, J. Org. Chem., 26, 3734 (1961); G.A. Russell, G.W. Holland, K.Y. Chang, R.G. Keske, J. Mattox, C.S.C. Chung, K. Stanley, K. Schmitt, R. Blankespoor and Y. Kosugi, J. Amer. Chem. Soc., 96, 7237 (1974).
13. E.J. Corey, R. Hartmann and R.A. Vatakencherry, J. Amer. Chem. Soc., 84, 2611 (1962).

(Received in USA 26 June 1978)