Olefin Synthesis by Two-fold Extrusion Processes. Part II.† Synthesis of Some Very Hindered Olefins

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Reaction of hindered thiones with hindered diazo-compounds affords Δ^3-1,3,4-thiadiazolines, which by two-fold extrusion afford in good yield very hindered olefins. In this way 2-diphenylmethylenebornane (VI), 2-diphenylmethylene-1,3,3-trimethylnorbornane (VIII), 1,1-di-t-butyl-2,2-diphenylethylene (XII), and 2-di-t-butylmethylenebornane have been prepared. The latter is probably the most hindered olefin prepared to date. The steric limitations of this approach have been explored. It was not possible to obtain in this way tetra-t-butylethylene (XIV) or 2-di-t-butylmethylene-1,3,3-trimethylnorbornane (XV).

In Part I of this series [1] we described a principle of olefin synthesis by two-fold extrusion of X and Y from a molecule of general formula (I) to give an olefin (II). This approach should be particularly suitable for the synthesis of hindered olefins.

The best procedure that we were able to develop was to make X = N=N and Y = S. Pyrolysis of Δ^3-1,3,4-thiadiazolines (III) under mild conditions gave first episulphides which, in the presence of a suitable phosphine, afforded olefins in good yield. This olefin synthesis was also developed independently by R. M. Kellogg and his collaborators.[2]

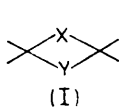
The general approach has been to treat a carbonyl compound with hydrazine and hydrogen sulphide (or to

† Part I, ref. 1*a*.

[1] (*a*) D. H. R. Barton and B. J. Willis, *J.C.S. Perkin I*, 1972, 305; (*b*) *Chem. Comm.*, 1970, 1225; D. H. R. Barton, E. H. Smith, and B. J. Willis, *ibid.*, p. 1226.

[2] R. M. Kellogg and S. Wassenaar, *Tetrahedron Letters*, 1970, 1987; R. M. Kellogg, S. Wassenaar, and J. Buter, *ibid.*, p. 4689; J. Buter, S. Wassenaar, and R. M. Kellogg, *J. Org. Chem.*, 1972, **37**, 4045.

add hydrogen sulphide to an azine) to give a 1,3,4-thiadiazolidine [as (IV)]. Mild oxidation of the latter at low temperature affords the Δ^3-1,3,4-thiadiazoline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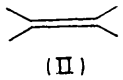
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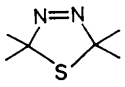
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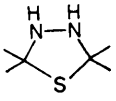

(IV)

(III). This procedure is well suited for the synthesis of moderately hindered tetra-substituted ethylenes which would be difficult to obtain in good yield by alternative methods. Several interesting applications of the synthesis have been reported.[3]

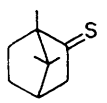
Some comparable experiments have been described on the addition of diazo-compounds to sulphines to afford Δ^3-1,3,4-thiadiazoline *S*-oxides. On pyrolysis, or spontaneously, episulphoxides are formed. From the latter olefins can be obtained.[4]

It has been our experience that very hindered olefins cannot be prepared through 1,3,4-thiadiazolidines [as (IV)], because the equilibrium between these compounds and the corresponding azine (plus hydrogen sulphide) lies too far on the side of dissociation. We have therefore considered an alternative route to the synthesis of Δ^3-1,3,4-thiadiazolines by the addition of a diazo-compound to a thione. This reaction has long been known [5,6,7] but its applicability for the synthesis of very hindered olefins has not so far been appreciated.

It is fortunate that thiones, which are often unstable and difficult to handle,[8] are more tractable the more hindered is the thione grouping. We describe first the synthesis of the needed thiones and relevant compounds.

Improved syntheses of diphenyldiazomethane, di-t-butyl ketone imine, di-t-butyl ketone *p*-tolylsulphonylhydrazone, and camphor hydrazone are reported in the Experimental section. From di-t-butyl ketone imine we prepared for the first time the stable di-t-butyl thioketone by the method of Ahmad and Lwowski.[9] Di-t-butyldiazomethane was prepared, also for the first time, from the ketone *p*-tolylsulphonylhydrazone and was a reasonably stable orange liquid. Its spectroscopic properties confirmed its structure even though a satisfactory microanalysis could not be obtained. (±)-Thiocamphor and (+)-thiofenchone had properties in agreement with the literature.[10]

(±)-Thiocamphor (V) reacted slowly with diphenyldiazomethane at room temperature to give an adduct. This rapidly lost nitrogen on heating in tetrahydrofuran to give a mixture of episulphides. This mixture was smoothly desulphurised with triphenylphosphine to furnish crystalline 2-diphenylmethylenebornane (VI) in excellent yield (Table). (+)-Thiofenchone (VII) gave in the same way crystalline 2-diphenylmethylenefenchane (VIII) (Table). These two results show the power of the two-fold extrusion process in the synthesis of very hindered olefins.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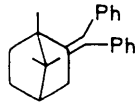
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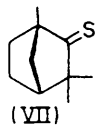
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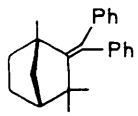
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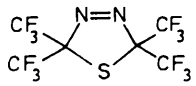
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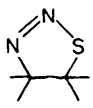
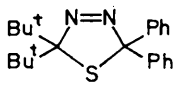

(X)

Although in one particular case (IX) the structure of the adduct from a thione and a diazo-compound has been established by n.m.r. considerations,[6] there is still uncertainty in the recent literature [7] as to whether the symmetrical [as (III)] or the unsymmetrical [as (X)] formula represents the normal case.

In a typical example we have proven that the symmetrical formula [as (III)] is correct in the following way. Di-t-butyl thioketone and diphenyldiazomethane at room temperature afforded a crystalline adduct which was thoroughly characterised. The *same* adduct was formed from thiobenzophenone and di-t-butyldiazomethane.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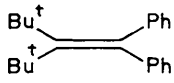
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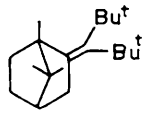

(XIII)

This is, of course, only possible if the adduct has the symmetrical structure (XI). Extrusion of nitrogen and of sulphur from this adduct (XI) gave the hindered olefin (XII) in satisfactory yield (Table).

Finally (±)-thiocamphor was treated with di-t-butyldiazomethane to give an adduct which on two-fold extrusion afforded the very hindered olefin (XIII) in

[3] J. W. Everett and P. J. Garratt, *J.C.S. Chem. Comm.*, 1972, 642; A. P. Schaap and G. R. Faler, *J. Org. Chem.*, 1973, **38**, 3061; H. Sauter, H. G. Hörster, and H. Prinzbach, *Angew. Chem. Internat. Edn.*, 1973, **12**, 991.

[4] B. Zwanenburg, L. Thijs, and J. Strating, *Tetrahedron Letters*, 1969, 4461; C. G. Venier and C. G. Gibbs, *ibid.*, 1972, 2293; B. Zwanenburg, A. Wagenaar, L. Thijs, and J. Strating, *J.C.S. Perkin I*, 1973, 73; B. F. Bonini and G. Maccagnani, *Tetrahedron Letters*, 1973, 3585.

[5] *Inter alia*, H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, 1920, **3**, 833; A. Schönberg, B. König, and E. Singer, *Chem. Ber.*, 1967, **100**, 767; C. E. Diebert, *J. Org. Chem.*, 1970, **35**, 1501; A. P. Krapcho, D. R. Rao, M. P. Silvon, and B. Abegaz, *ibid.*, 1971, **36**, 3885.

[6] W. J. Middleton, *J. Org. Chem.*, 1969, **34**, 3201.

[7] J. M. Beiner, D. Lecadet, D. Paquer, A. Thuillier, and J. Vialle, *Bull. Soc. chim. France*, 1973, 1979, 1983; P. Metzner, *ibid.*, p. 2297.

[8] R. Mayer, J. Morgenstern, and J. Fabian, *Angew. Chem. Internat. Edn.*, 1964, **3**, 277.

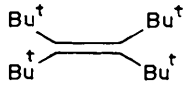
[9] R. Ahmed and W. Lwowski, *Tetrahedron Letters*, 1969, 3611; H. B. Williams, K. N. Yarbrough, K. L. Crocket, and D. V. Wells, *Tetrahedron*, 1970, **26**, 817.

[10] D. C. Sen, *J. Indian Chem. Soc.*, 1935, **12**, 647; 1937, **14**, 214.

satisfactory yield (Table). In this case the desulphurisation step was better accomplished using the more reactive tributylphosphine.

The very hindered olefins prepared (Table) have been fully characterised by microanalysis and by physical methods and there can be no doubt as to their structures. It was not possible to cleave the olefinic double bonds by standard oxidising procedures. These hindered double bonds were inert to procedures such as ozonolysis, and stronger oxidising conditions simply led to degradation.

We examined the steric limits to our approach to very hindered olefins with two particular objectives in mind, namely, tetra-t-butylethylene (XIV) and 2-di-t-butylmethylenefenchane (XV). We could obtain no evidence for the formation of either of these compounds by



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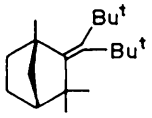

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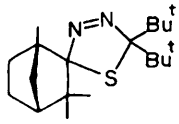
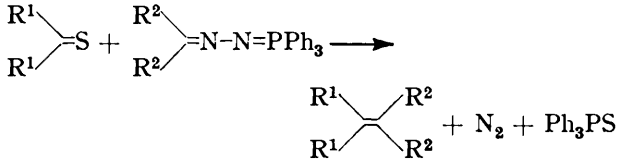


(XVI)

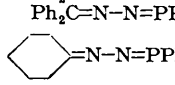
the methodology developed above and their synthesis remains an interesting challenge for the future.

During the course of these unsuccessful experiments we attempted to cause (+)-thiofenchone (VII) to react with di-t-butyldiazomethane by prolonged heating under reflux in tetrahydrofuran. The only identifiable product was di-t-butyl thioketone. The formation of this 'exchange' product would seem to suggest that the desired adduct (XVI) was indeed formed, but that it reversed faster than it lost nitrogen to give episulphide. The complex product mixture from the reaction was, therefore, derived from the thermal decomposition products of 2-diazofenchane and di-t-butyldiazomethane.

We have also considered an alternative approach to the synthesis of sterically hindered olefins in which a trivalent phosphine is incorporated into the reagent in such a way as to be released during reaction. The obvious procedure would be to treat a thione with a triphenylphosphoranediylhydrazone according to equation (1):

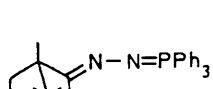


The results obtained are summarised in the Table. Reaction of (±)-thiocamphor with benzophenone triphenylphosphoranediylhydrazone, or of thiobenzophenone with (±)-camphor triphenylphosphoranediylhydrazone, (XVII) gave the olefin (VI) in reasonable yield. Similarly, reaction of (+)-thiofenchone or of di-t-butyl thioketone and benzophenone triphenylphosphoranediylhydrazone gave the olefins (VIII) and (XII) in similar yield. The latter was optimised. It is clear that the phosphoranediylhydrazone route, although a one-step procedure, gives less satisfactory results than the two-step procedure through a diazo-compound. The temperature of reaction is also higher.

Thione	Diazo-compound or phosphoranediyl-hydrazone	Phosphine	Olefin produced	Yield (%)
(V)	Ph_2CN_2	Ph_3P	(VI)	90
(VII)	Ph_2CN_2	Ph_3P	(VIII)	90
But_2CS	Ph_2CN_2	Ph_3P	(XII)	68
Ph_2CS	But_2CN_2	Ph_3P	(XII)	69
(V)	But_2CN_2	Bu_3P	(XIII)	64
(V)	$Ph_2C{=}N{-}N{=}PPh_3$	?PPh_3	(VI)	67 †
Ph_2CS	(XVII)	?PPh_3	(VI)	46 †
(VII)	$Ph_2C{=}N{-}N{=}PPh_3$	?PPh_3	(VIII)	44 †
But_2CS	$Ph_2C{=}N{-}N{=}PPh_3$	?PPh_3	(XII)	63 *
(VII)		?PPh_3	(XVIII)	47 †

* Isolated yield of recrystallised or sublimed olefin. † Approximate yields not optimised.

The mechanism of the phosphoranediylhydrazone process probably involves the *in situ* dissociation of the hydrazone into diazo-compound and triphenylphosphine



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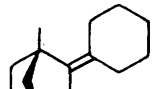
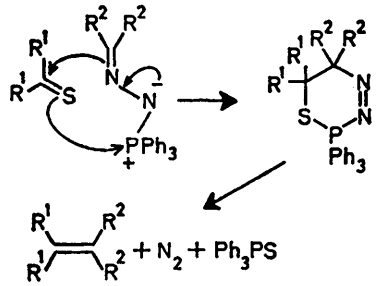


(XVIII)

followed by the usual sequence of reactions. There may however, be an alternative mechanism such as the following (or its equivalent):



The evidence at hand does not permit us to distinguish between these alternatives.

Finally, we also examined the possibility of generating the phosphoranediylhydrazone *in situ*. Cyclohexanone *p*-tolylsulphonylhydrazone was treated with sodium hydride and triphenylphosphine at 120—130° to form cyclohexanone triphenylphosphoranediylhydrazone. (+)-Thiofenchone was then added and the temperature raised to 180—185°. This afforded the olefin (XVIII) in reasonable yield.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were recorded with a Unicam SP 200 spectrometer and u.v. spectra with a Unicam SP 800B spectrometer. ^1H N.m.r. spectra were recorded with a Varian T60 instrument (tetramethylsilane as an internal reference).

Mass spectra were recorded with an A.E.I. MS9 or a Perkin-Elmer 270 instrument. Rotations were measured on a Perkin-Elmer 141 polarimeter. Satisfactory spectral data were obtained for all compounds and only typical spectra are recorded. Organic solutions were washed with saturated sodium chloride and dried over anhydrous sodium sulphate before concentration. ' Light petroleum ' refers to the fraction b.p. 40—60°, and ' petroleum ' to the fraction b.p. 60—80°.

Benzophenone Hydrazone.—Benzophenone (36·4 g) and hydrazine hydrate (30 ml) in diethylene glycol (70 ml) were refluxed for 16 h, poured onto cold water (300 ml), and the mixture scratched until crystals formed. Recrystallisation from aqueous ethanol afforded the hydrazone (87%), m.p. 97—98° (lit.,[11] 97—98°).

Diphenyldiazomethane (With B. J. Willis).—Lead tetra-acetate (889 mg) in dichloromethane (5 ml) was added dropwise over 45 min to a stirred solution of benzophenone hydrazone (295 mg) in dichloromethane (4 ml) and triethylamine (5 ml) at −20°, with the immediate appearance of the crimson diazo-compound. The solution was allowed to warm to 20°, solid was removed by filtration through Celite, and the organic layer was washed with water and dried. Evaporation of the solvent gave diphenyldiazomethane as a crimson solid (100%), identical with a sample prepared by mercuric oxide oxidation.

Di-t-butyl Ketone Imine.—Pivalonitrile (33·2 g) and t-butyl chloride (44·4 g) were added under nitrogen over 1 h to a well-stirred suspension of sodium sand [12] (18·4 g) in a mixture of light petroleum (80 ml), tetrahydrofuran (20 ml), and methanol (1 ml) keeping the reaction temperature between 15 and 20° during addition. The mixture was stirred 3 h, chlorobenzene (2 g) in tetrahydrofuran (5 ml) was added dropwise over 10 min, and stirring continued (1 h). Methanol (20 ml) was cautiously added over 0·5 h, followed by water, until clear phases separated. The organic phase was separated, and the aqueous phase extracted with ether (3 × 50 ml). The combined organic phases were dried and concentrated under reduced pressure. Distillation afforded pure imine (63%), b.p. 62—63° at 19 mmHg (lit.,[13] 78·5—80° at 50 mmHg).

Di-t-butyl Ketone p-*Tolylsulphonylhydrazone.*—Di-t-butyl ketone imine (7·07 g), *p*-tolylsulphonylhydrazine (10·24 g), and glacial acetic acid (3·1 ml) in dry dichloromethane (20 ml) were heated to reflux under nitrogen for 16 h. The mixture was diluted with dichloromethane (40 ml), and washed with water, dilute hydrochloric acid, and dried. Removal of solvent under reduced pressure and recrystallisation of the residue from chloroform–light petroleum afforded the hydrazone (60%), m.p. 176—177° [lit.,[13] 177—179° (decomp.)].

Alternatively, di-t-butyl ketone hydrazone [13] was treated with toluene-*p*-sulphonyl chloride in pyridine in the usual way to give the same derivative in no better yield.

Di-t-butyldiazomethane.—Di-t-butyl ketone *p*-tolylsulphonylhydrazone (1·55 g) was added in small portions to a stirred suspension of sodium hydride (150 mg; 80%) in dry tetrahydrofuran (10 ml). When evolution of hydrogen had ceased the solution was heated under reflux under nitrogen for 3 h, the solvent was removed at room temperature under reduced pressure, and the residue distilled at room temperature *in vacuo* into a solid CO_2–acetone trap, affording the diazo-compound as an orange liquid (*ca.* 90%), $\nu_{max.}$ (CCl_4) 2060, 1395, and 1375 cm^{-1}, δ (CCl_4) 1·25 (s).

Di-t-butyl Thioketone.—Di-t-butyl ketone imine (5·64 g) in dry light petroleum under dry nitrogen was treated with ethereal methyl-lithium (1·00 mol. equiv.). When methane evolution had ceased, dry carbon disulphide [9] (3·2 ml) was added and the mixture stirred for 3 h. Solvent was removed under reduced pressure at room temperature, and the solid brown residue heated at 80—100° under vacuum while practically pure thione distilled into a solid CO_2–acetone trap (100%). The residue is yellow when the distillation is complete. Redistillation afforded pure, deep violet *thioketone*, b.p. 61° at 14 mmHg, $\nu_{max.}$ (film) 1400, 1365, and 1120 cm^{-1}, δ (CCl_4) 1·5 (s), *m/e* 150 (M^+) (Found: C, 68·5; H, 11·2; S, 19·9. $C_9H_{18}S$ requires C, 68·3; H, 11·5; S, 20·2%).

(−)-*Thiocamphor.*—(+)-Camphor (15·2 g) and trimethyl orthoformate (15·9 g) in dry methanol (50 ml) were cooled to 0° and simultaneously saturated with streams of hydrogen sulphide and hydrogen chloride gas over 1·5 h. Pouring onto ice (200 ml) afforded orange crystals of crude thione. Traces of ketone were removed by dissolving the thione in warm petroleum and chromatography on silica gel (10 g) (elution with petroleum). Concentration under reduced pressure and sublimation at 85° and 20 mmHg afforded pure thione (88%), m.p. 145—146° (lit.,[10] 146°), $[\alpha]_D^{24}$ −21·4° (*c*, 3·0 in EtOAc).

(±)-Thiocamphor was prepared analogously (85%), m.p. 145—146° (lit.,[10] 145—146°).

(+)-*Thiofenchone.*—(+)-Fenchone (97%) (15·2 g) and trimethyl orthoformate (11·7 g) in dry methanol (100 ml) were cooled to 0° and simultaneously saturated with streams of hydrogen sulphide and hydrogen chloride gas over 1·5 h. The stoppered mixture was allowed to come to room temperature over 1 h, poured into ether (100 ml) and water (150 ml), and the ether layer was washed with water until neutral, dried, and concentrated. The crude thione was chromatographed on silica gel (10 g) (eluted with petroleum). Distillation afforded deep orange crystals of (+)-thiofenchone (88%), m.p. 22—24°, b.p. 105° at 15 mmHg (lit.,[10] 92° at 5 mmHg), $[\alpha]_D^{21}$ +46·1° (*c*, 1·2 in EtOAc).

(+)-*Camphor* p-*Tolylsulphonylhydrazone.*—(+)-Camphor (15·2 g) and *p*-tolylsulphonylhydrazine (18·6 g) in ethanol (60 ml) were heated until homogenous, concentrated hydrochloric acid (2 ml) was added, and the solution heated under reflux for 1 h to give, on cooling, the hydrazone (67%), m.p. 159—162°, $[\alpha]_D^{22}$ +12·1 (*c* 2·9 in EtOH). Heating the mother liquors under reflux for an additional 1 h and diluting with water afforded an additional crop (13%), m.p. 157—162°. The crude hydrazone could be used without further purification. Recrystallisation from aqueous ethanol afforded the *hydrazone* as needles, m.p. 161—162°, $[\alpha]_D^{21}$ +13·1 (*c*, 2·5 in EtOH), $\nu_{max.}$ ($CHCl_3$) 1660 and 1600 cm^{-1}, *m/e* 320 (M^+) (Found: C, 63·9; H, 7·6; N, 8·6; S, 10·0. $C_{17}H_{24}N_2SO_2$ requires C, 63·7; H, 7·6; N, 8·7; S, 10·0%).

(±)-Camphor *p*-tosylhydrazone, m.p. 161—164° (lit.,[14] 163—164°), could be prepared analogously (78%).

Camphor Hydrazone.—(±)-Camphor (15·5 g) and hydrazine hydrate (14 g) in diethylene glycol (20 ml) and ethanol (4 ml) were heated under reflux overnight (mixture becomes homogenous). The cooled solution was poured into water

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(150 ml) and extracted with benzene–hexane (1 : 1) (3 × 40 ml). The combined organic phase was washed with water (2 × 10 ml) and then with ice-cold water (50 ml) containing concentrated HCl (10 ml). The aqueous phase was separated as quickly as possible into water (120 ml) containing potassium carbonate (40 g) and covered with a layer of benzene–hexane (1 : 1). The organic phase was separated, dried over K_2CO_3, filtered, and evaporated to give (±)-camphor hydrazone (14·1 g, 83%), m.p. 55°.

(±)-2-*Diphenylmethylenecamphane* (VI).—Diphenyldiazomethane (582 mg) and (±)-thiocamphor (505 mg) in dry tetrahydrofuran (5 ml) were heated under reflux under nitrogen for 3 h. Solvent removal and chromatography on silica gel (20 g, light petroleum) afforded a crude crystalline episulphide mixture (*ca.* 100%), m.p. 78—105°. The episulphide and triphenylphosphine (870 mg) in tetrahydrofuran (5 ml) were refluxed under nitrogen for 16 h, and the solvent was removed under reduced pressure, and the residue dissolved in petroleum (30 ml) and carefully treated with iodomethane (1 ml) (very exothermic). After stirring for 2 h the petroleum solution was decanted onto a silica gel column (5 g) and pure olefin eluted with light petroleum. Solvent removal and recrystallisation of the crude olefin from warm aqueous ethanol (in two crops) afforded crystals (90%), m.p. 69·5—72·5° of (±)-2-*diphenylmethylenecamphane* [(±)-2-*diphenylmethylenebornane*] (VI). Recrystallised this had m.p. 71·5—73°, $\nu_{max.}$ (CCl_4) 1600, 1500, 1480, and 1460 cm^{-1}, $\lambda_{max.}$ 244 nm (ε 11,000), *m/e* 302 (M^+) (Found: C, 91·1; H, 8·6. $C_{23}H_{26}$ requires C, 91·3; H, 8·65%).

(+)-2-*Diphenylmethylenefenchane* (VIII).—The olefin was prepared by a procedure analogous to that used for the camphor derivative on a 6 mmol scale without isolation of episulphides. Recrystallisation of the crude olefin from aqueous ethanol in two crops afforded (+)-2-*diphenylmethylenefenchane* [(+)-2-*diphenylmethylene*-1,3,3-*trimethylnorbornane*] (VIII) (90%), m.p. 137—139° (subl.) $[\alpha]_D^{24}$ 29·9° (*c*, 1·2 in EtOH). Recrystallised this had m.p. 137—139° (subl.), $[\alpha]_D^{23}$ +37·7° (*c*, 0·9 in EtOH), $\nu_{max.}$ (CCl_4) 1600, 1500, 1385, and 1365 cm^{-1}, $\lambda_{max.}$ (EtOH) 225 nm (ε 12,000), *m/e* 302 (M^+) (Found: C, 91·3; H, 8·7. $C_{23}H_{26}$ requires C, 91·3; H, 8·65%).

1,1-*Di-t-butyl*-2,2-*diphenylethylene* (XII).—(*a*) Prepared according to the general procedure from diphenyldiazomethane and di-t-butyl thioketone, 1,1-*di-t-butyl*-2,2-*diphenylethylene* (XII) (68%) had (two crops from aqueous ethanol), m.p. 137—139° (subl.). A further recrystallisation afforded pure olefin m.p. 140·5—141° (subl.), $\nu_{max.}$ (CCl_4) 1600, 1490, 1440, 1400, and 1370 cm^{-1}, δ (CCl_4) 7·05 (10H, complex) and 1·15 (18H, s), $\lambda_{max.}$ (EtOH) 242 nm (ε 13,000), *m/e* 292 (M^+), 236 ($M - C_4H_8$), and 235 ($M - C_4H_9$) (Found: C, 90·3; H, 9·7. $C_{22}H_{28}$ requires C, 90·4; H, 9·6%).

(*b*) Thiobenzophenone (0·89 g) was added to a stirred solution of di-t-butyldiazomethane in tetrahydrofuran [from tosylhydrazone (1·55 g)] resulting in immediate decolourisation. Triphenylphosphine (1·31 g) was added, and the mixture refluxed for 15 h. Work-up in the usual manner afforded the olefin (XII) (69%), two crops from aqueous ethanol, m.p. 137—139° (subl.), identical with that prepared in (*a*).

(±)-2-*Di-t-butylmethylenecamphane* (XIII).—(±)-Thiocamphor (505 mg) and di-t-butyldiazomethane [from tosylhydrazone (1·02 g)] in tetrahydrofuran (5 ml) were heated to reflux under nitrogen for 15 h. The mixture was filtered, solvent removed under reduced pressure, and the crude episulphide mixture treated with tri-n-butylphosphine (3 ml) and heated at 120° under nitrogen for 15 h. The mixture was treated with iodomethane (3 ml) in petroleum (30 ml) (very exothermic), stirred 2 h, filtered, and concentrated. Column chromatography on silica (5 g) (elution with petroleum) afforded the crude olefin (64%). Traces of (±)-2-(bornan-2-ylidene)bornane were removed by sublimation at 80° (0·5 mmHg) onto a solid CO_2–acetone cold-finger affording crystals of (±)-2-*di-t-butylmethylenecamphane* [(±)-2-*di-t-butylmethylenebornane*] (XIII), which melted upon warming to room temperature, $\nu_{max.}$ (CCl_4) 1395 and 1370 cm^{-1}, *m/e* 262 (M^+), 206 ($M - C_4H_8$), and 205 ($M - C_4H_9$) (Found: C, 86·7; H, 13·0. $C_{19}H_{34}$ requires C, 86·9; H, 13·1%).

2,2-*Di-t-butyl*-5,5-*diphenyl*-Δ³-1,3,4-*thiadiazoline* (XI).—(*a*) Diphenyldiazomethane (582 mg) and di-t-butyl thioketone (477 mg) in dry ether (5 ml) were left at room temperature for 2·5 h (slight yellow colour) and then cooled to 4°. Prisms of the *thiadiazoline* (XI) slowly separated (25%), m.p. 118—120° (decomp.), $\nu_{max.}$ (CCl_4) 2050, 1600, 1585, 1400, and 1375 cm^{-1} (no 2050 cm^{-1} band in Nujol), δ (CCl_4) 7·8—7·05 (10H, complex) and 1·05 (18H, s), $\lambda_{max.}$ (EtOH) 314 (ε 2000), 264sh (1500), and 224 nm (13,000). Evaporation of the mother liquor and trituration of the residue with cold ether–light petroleum (1 : 1) afforded an additional crop of thiadiazoline (46%; 71% total). Solutions of the thiadiazoline in carbon tetrachloride, chloroform, and dichloromethane are deep blue, but colourless in ether, ethanol, and tetrahydrofuran (Found: C, 75·1; H, 7·9; N, 8·0; S, 9·2. $C_{22}H_{28}N_2S$ requires C, 75·0; H, 8·0; N, 8·0; S, 9·1%).

(*b*) Thiobenzophenone (*ca.* 590 mg) was added in small portions to a stirred solution of di-t-butyldiazomethane [from tosylhydrazone (1·02 g)] in ether (5 ml) until a blue colour persisted for 1 min. Upon cooling the mixture afforded prisms (7%), identical with those formed in (*a*), by m.p., mixed m.p., and n.m.r. and i.r. spectra. Concentration of the mother liquors and trituration of the residue with cold ether–light petroleum afforded more thiadiazoline (49%; 56% total), m.p. 115—120° (decomp.)

Attempted Cleavage of the Ethylene (XII).—(a) *By ozonolysis.* Ozone was bubbled for 30 min through a solution of the ethylene (XII) (146 mg) in dry dichloromethane (10 ml) kept at −30°. No reaction was observed on t.l.c. The temperature was raised to 25° and ozone passed into the mixture for 2 h. Flushing with oxygen and solvent removal afforded only unchanged olefin.

(b) *By permanganate–periodate oxidation.* The ethylene (XII) (146 mg), potassium permanganate (150 mg), sodium periodate (1 g), and potassium carbonate (50 mg) in acetone (40 ml) and water (10 ml) were heated to reflux overnight. At 19 h the mixture was filtered and extracted with ether. The ethereal solution was dried and concentrated, affording only the crystalline olefin in nearly quantitative yield.

(c) *With chromic acid.* To the ethylene (XII) (146 mg) in glacial acetic acid (2 ml) was added a solution of chromic anhydride (190 mg) in acetic acid (0·35 ml) and water (0·15 ml). A slow reaction was observed and the reaction continued until no olefin was observed on t.l.c. (3 days). Excess of chromic acid was destroyed with sodium bisulphite and the mixture extracted with dichloromethane. The extract was dried and concentrated affording a complex mixture as a yellow oil (150 mg). Neither di-t-butyl ketone nor benzophenone could be detected in the mixture (i.r. and n.m.r. spectra, t.l.c.).

Attempted Preparation of 2-Di-t-butylmethylenefenchane (XV).—(+)-Thiofenchone (0·84 g) and di-t-butyldiazomethane (5·5 mmol) in dry tetrahydrofuran (10 ml) were heated to reflux under nitrogen for 16 h. Concentration under reduced pressure at room temperature and chromatography (silica, light petroleum) afforded di-t-butyl thioketone (20%) and no sign of 2-di-t-butylmethylenefenchane or of its episulphide.

Attempted Preparation of Tetra-t-butylethylene (XIV).—Di-t-butyl thioketone (0·47 g) and di-t-butyldiazomethane (3·3 mmol) in dry tetrahydrofuran (10 ml) were heated to reflux under nitrogen for 40 h. (A significant amount of diazo-compound remained.) No new products (aside from diazo-compound decomposition products) were observed (t.l.c., and n.m.r. and i.r. spectra).

The thione (0·47 g) and diazo-compound (3·3 mmol) were heated neat to 120° under nitrogen for 2 h affording a complex mixture (complete disappearance of diazo-compound). Separation of products by preparative t.l.c. afforded no significant amounts of tetra-t-butylethylene or of its episulphide (n.m.r., i.r., and mass spectra).

Alternative Syntheses of (±)-*2-Diphenylmethylenecamphane* (V).—(a) *From benzophenone triphenylphosphoranediylhydrazone.* Benzophenone triphenylphosphoranediylhydrazone[15] (640 mg) and (±)-thiocamphor (220 mg) in dry dimethylacetamide (5 ml) were heated under reflux at 185° (bath temperature) for 25 min. The solution was poured into 6N-HCl (20 ml) and benzene (20 ml). The benzene layer was separated, washed with aquous $NaHCO_3$, dried ($MgSO_4$), and evaporated. The residue was digested with hexane leaving triphenylphosphine sulphide (223 mg). The hexane extract was filtered through silica to give (±)-2-diphenylmethylenecamphane (67%).

(b) *From* (±)-*camphor triphenylphosphoranediylhydrazone.* The (±)-camphor derivative[15] (426 mg) and thiobenzophenone (200 mg) in dry dimethylacetamide (5 ml) were heated under reflux for 10 min at 185° (bath temperature). The solution was worked up as above to give (±)-2-diphenylmethylenebornane (46%).

Alternative Synthesis of 2-Diphenylmethylenefenchane (VIII).—Benzophenone triphenylphosphoranediylhydrazone (1·8 g) and (+)-thiofenchone (321 mg) in dry dimethylacetamide (7 ml) were heated under reflux for 15 min at 180—185° (bath temperature). The solution was worked up as above to give, after crystallisation from MeOH–EtOH (1 : 1), (+)-2-diphenylmethylenefenchane (VIII) (44%).

Alternative Synthesis of 1,1-*Di-t-butyl*-2,2-*diphenylethylene* (XII).—Benzophenone triphenylphoranediylhydrazone[15] (1·00 g) and di-t-butyl thioketone (0·32 g) in dry triethylamine (3 ml) were heated to reflux under positive nitrogen pressure until no hydrazone remained (70 h). Removal of solvent under reduced pressure, column chromatography (silica, petroleum), and crystallisation (two crops from aqueous ethanol) afforded the olefin (XII) (63%), m.p. 140—141° (subl.). A reaction using dry benzene as solvent afforded the olefin (XII) in 31% yield; dry benzene plus triphenylphosphine (1 or 3 mol. eq.) afforded the olefin in 49 and 55% yield respectively.

2-*Cyclohexylidenefenchane* (XVIII).—Cyclohexanone *p*-tolylsulphonylhydrazone (670 mg) and triphenylphosphine (3·3 mmol) were added to benzene-washed sodium hydride (60%; 130 mg) suspended in dry dimethylacetamide (5 ml) and the mixture was stirred at 120—130° (bath temperature) for 20 min. (+)-Thiofenchone (475 mg) in dimethylacetamide (5 ml) was added and the solution heated under reflux at 180—185° (bath temperature) for 40 min. The solution was worked up as above to give an oil (437 mg). Distillation at 145—150° at 20 mmHg gave 2-*cyclohexylidenefenchane* (2-*cyclohexylidene*-1,3,3-*trimethylnorbornane*) (XVIII) (47%) (Found: C, 88·3; H, 11·7. $C_{16}H_{26}$ requires C, 88·0; H, 12·0).

We thank the S.R.C. for financial assistance.

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[4/593 *Received*, 25*th March*, 1974]