Synthesis of Olefins by Base-induced Fragmentation of 2-Phenyl-1,3-oxathiolans

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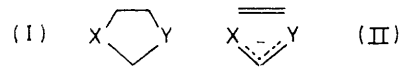
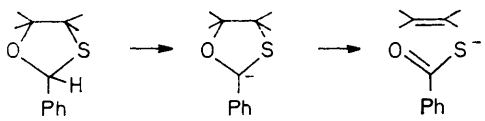
Treatment of 2-phenyl-1,3-oxathiolans with a lithium dialkylamide in ether leads to fragmentation to olefin and lithium thiobenzoate. Under certain conditions further reaction to give a dialkylbenzamide occurs. The olefin is formed stereospecifically, and the reaction has been developed into a method for ' olefin inversion,' illustrated by the preparation of *trans*-cyclo-octene, *cis,trans*-cyclo-octa-1,5-diene, and *cis*-stilbene. The latter two examples represent structural types which could not be prepared by the dioxolan olefin synthesis.

In an earlier paper [1] we considered heteroanion fragmentations of the type (I) ⟶ (II) in general, and in particular discussed the scope and limitations of an olefin synthesis involving cycloelimination reactions of lithiated 2-phenyl-1,3-dioxolans. Although such reactions have some applicability, particularly to a convenient synthesis of *trans*-cyclo-octene, they are not successful for tri- and tetra-substituted olefins, for styrenes, stilbenes, *etc.*, nor for highly strained olefins such as *cis,trans*-cyclo-octa-1,5-diene. These limitations stem essentially from the relatively low acidity of the C-2 proton in a 2-phenyl-1,3-dioxolan. Thus, either the strong bases required for deprotonation have undesirable side effects, or, in the heavily alkylated substrates, proton abstraction does not occur at all. In an attempt to remedy some of these deficiencies we have explored the possibility of fragmenting 2-phenyl-1,3-oxathiolans. Although we have only investigated a small range of substrates, it is clear that the oxathiolan route is of considerable potential and can be applied to the synthesis of olefins inaccessible by the dioxolan approach.



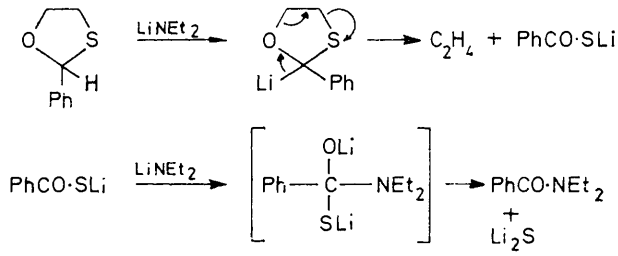
The essential reaction under investigation is shown in Scheme 1. It was hoped that, in comparison with the



Scheme 1

corresponding dioxolans, the C-2 proton would be appreciably more acidic, owing to the influence of adjacent sulphur.[2] An additional attractive feature was that thiobenzoate might be a better leaving group than benzoate ion.†

In preliminary experiments with 2-phenyl-1,3-oxathiolan, vigorous reaction occurred, as expected, with n-butyl-lithium in hexane. More important from the synthetic point of view was the discovery that this oxathiolan reacted rapidly with lithium diethylamide in ether with evolution of gas (ethylene ?) and formation of *NN*-diethylbenzamide. Two mol. equiv. of amide were required for consumption of all the oxathiolan. Apparently the reaction of lithium diethylamide with lithium thiobenzoate is faster than proton abstraction from oxathiolan. The probable reaction pathway is shown in Scheme 2.



Scheme 2

To evaluate more quantitatively the reaction of lithium dialkylamides with 2-phenyl-1,3-oxathiolans, we chose 2,5-diphenyl-1,3-oxathiolan as substrate since the styrene produced by fragmentation could be monitored by u.v. spectroscopy. Some of the results are summarised in the Table. Good yields of styrene were

Fragmentation of 2,5-diphenyl-1,3-oxathiolan [a]

Base : oxathiolan mol. ratio	Yield (%) Styrene [b]	Thiobenzoate [b]
1·0 : 1 [c]	45	
2·23 : 1 [c]	89	
4·2 : 1 [c]	97	
1·4 : 1 [d]	99	70
3·2 : 1 [d]	99	22

[a] 15 min at 20° in Et_2O. [b] By u.v. spectroscopy. [c] Lithium diethylamide as base. [d] Lithium cyclohexylisopropylamide as base.

obtained with lithium diethylamide as base provided that at least 2 mol. equiv. of base were used; the other product was diethylbenzamide. With lithium cyclohexylisopropylamide [4] as base a good yield of styrene was obtained even with 1·4 mol. equiv., and thiobenzoate ion was detected in appreciable amount. Clearly, with the more hindered base attack on lithium thiobenzoate is slower, and this step no longer competes efficiently with proton abstraction from the oxathiolan.

† *Cf.* respective pK_a (H_2O) values: benzoic acid 4·21, thiobenzoic acid 2·66.[3]

[1] J. N. Hines, M. J. Peagram, E. J. Thomas, and G. H. Whitham, *J.C.S. Perkin I*, 1973, 2332.

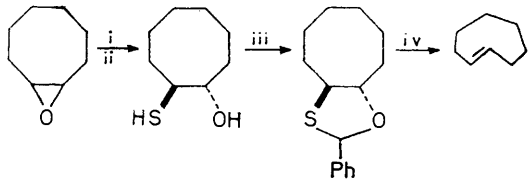
[2] *Cf.* G. Cilento, *Chem. Rev.*, 1960, **60**, 147.

[3] J. Juillard, *Bull. Soc. chim. France*, 1966, 1727.

[4] M. W. Rathke and A. Lindert, *J. Amer. Chem. Soc.*, 1971, **93**, 2318.

To develop this fragmentation into a useful olefin synthesis it is necessary to have a good, preferably stereospecific route to mercaptoethanols. Although a variety of routes depending on the opening of epoxides with sulphur nucleophiles have been known for some time [5] they are not generally applicable to less reactive epoxides, or epoxides prone to rearrangement under acidic conditions. However, a recent paper [6] describes the stereospecific conversion of epoxides into 2-mercapto-alcohols (with a single inversion) *via* reaction with sulphurated borohydride followed by reduction of the resulting disulphide with lithium aluminium hydride. We have found this reaction to be convenient and effective.

To test the overall stereospecificity of the process: epoxide ⟶ mercaptoalcohol ⟶ oxathiolan ⟶ olefin we carried out the conversion of *cis*-1,2-epoxycyclo-octane into *trans*-cyclo-octene as summarised in Scheme 3. For the routine preparation of *trans*-cyclo-octene

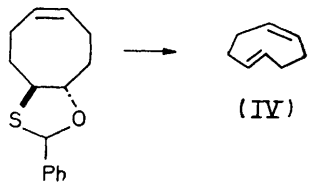


SCHEME 3

Reagents: i, $NaBH_2S_3$; ii, $LiAlH_4$; iii, PhCHO–H^+ iv, $LiNR_2$

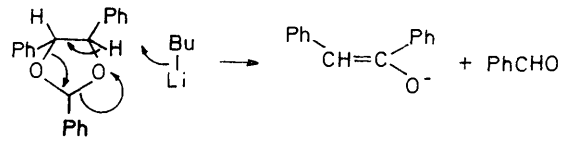
however, the dioxolan synthesis [1] is experimentally more convenient.

A more stringent test of the synthetic viability of the oxathiolan fragmentation is provided by the formation of the sensitive *cis,trans*-cyclo-octa-1,5-diene [7] * (IV) on treatment of the oxathiolan (III) with lithium diethylamide in ether. Attempts to prepare this diene from the analogous dioxolan with n-butyl-lithium had earlier led only to products derived from addition of n-butyl-lithium to the diene.[1]



(III) (IV)

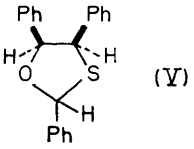
Another situation in which the dioxolan fragmentation had proved deficient as an olefin synthesis was in the case of phenyl substitution at C-4 (C-5). Thus the isomeric 2,4,5-triphenyl-1,3-dioxolans underwent predominant fragmentation initiated by proton abstraction from C-4. It was therefore of interest to investigate fragmentation of the 2,4,5-triphenyloxathiolan (V) obtained from the mercaptoalcohol derived by opening *trans*-stilbene epoxide with sulphurated borohydride.[6]



In this oxathiolan (V) proton abstraction could, in principle, occur from C-2, C-4, or C-5. Although the last possibility was unlikely, owing to the absence of adjacent sulphur, it was difficult to decide between the other two because of doubts about the influence of the oxygen atom on the acidity of the C-2 proton. Analogy with the dioxolan case (see above) might have predicted that products derived from attack on the proton at C-4 would predominate.

In fact the major product from treatment of the oxathiolan (V) with lithium cyclohexylisopropylamide in ether was *cis*-stilbene (71%). Only small amounts of deoxybenzoin, considered to have been derived from benzyl phenyl thioketone by exposure to the atmosphere, were detected. Evidently the most important cyclo-elimination process is that initiated by proton abstraction from C-2.

Finally we have investigated the possibility of the formation of a tetrasubstituted olefin, bearing in mind that in the dioxolan work 4,4,5,5-tetramethyl-2-phenyl-1,3-dioxolan was recovered unchanged from treatment



(V)

with n-butyl-lithium.[1] Treatment of 4,4,5,5-tetramethyl-2-phenyl-1,3-oxathiolan with lithium diethylamide in ether gave tetramethylethylene, characterised as its dibromide. Clearly the metallation–fragmentation of 2-phenyloxathiolans is less susceptible to steric and/or conformational deactivating influences than fragmentation of the analogous dioxolans. Presumably such influences are relatively less important in the more acidic oxathiolan system.

We have not carried out any detailed mechanistic investigations on this reaction, but we currently favour a pre-equilibrium metallation of the oxathiolan followed by rate- (and product-) determining fragmentation. In these terms, the preferred formation of *cis*-stilbene from the oxathiolan (V) can be explained by departure of thiobenzoate ion as the better leaving group.

In summary, the fragmentation of 2-phenyl-1,3-

* For a recent preparation of this diene by the phosphorus betaine method of Vedejs, see ref. 8.

[5] A. Rosowsky, in ' Heterocyclic Compounds with Three- and Four-membered Rings,' ed. A. Weissberger, Interscience, 1964, p. 327.

[6] J. M. Lalancette and A. Frêche, *Canad. J. Chem.*, 1971, **49**, 4047.

[7] A. C. Cope, C. F. Howell, J. Bowers, R. C. Lord, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1967, **89**, 4024.

[8] E. Vedejs, K. A. J. Snoble, and P. L. Fuchs, *J. Org. Chem.*, 1973, **38**, 1178.

oxathiolans by lithium dialkylamide in ether provides a convenient stereospecific route to certain types of olefin which could not be obtained by treatment of the analogous dioxolans with n-butyl-lithium. In particular, we find this preparation of *cis,trans*-cyclo-octa-1,5-diene to be the most convenient way of obtaining reasonable quantities (10—20 g) of this reactive diene.

EXPERIMENTAL

Unless otherwise stated n.m.r. spectra were obtained for solutions in CCl_4 with Perkin-Elmer R10 (60 MHz) or R14 (100 MHz) instruments.

2,5-Diphenyl-1,3-oxathiolan.—A solution of 2-mercapto-1-phenylethanol [9] (2·14 g, 0·014 mol) and purified benzaldehyde (1·47 g, 0·014 mol) in dry benzene (50 ml) containing toluene-*p*-sulphonic acid (0·005 g, 0·01%) was heated under reflux (Dean–Stark head) until no more water was produced (40 min). The benzene solution was washed with aqueous potassium hydroxide (2N), and after drying and evaporation, traces of benzaldehyde were removed by maintaining the product at 100° and 0·07 mmHg for 1 h. The *oxathiolan* was obtained as an oil (2·6 g, 76%), b.p. 190° at 0·5 mmHg (decomp.) (Found: C, 73·6; H, 6·0; S, 13·75. $C_{13}H_{14}OS$ requires C, 74·35; H, 5·85; S, 13·2%), $\tau_{max.}$ 3·78 and 3·91 (benzylic proton) (indicating the presence of two diastereoisomers in the ratio 1 : 4).

trans-2-*Mercaptocyclo-octanol.*—Dry tetrahydrofuran (THF) (80 ml) was added rapidly to an ice-cooled mixture of sulphur (9·6 g, 0·3 mol) and sodium borohydride (3·8 g, 0·1 mol) under nitrogen. After evolution of hydrogen had ceased (15 min), *cis*-1,2-epoxycyclo-octane [10] (6·3 g, 0·05 mol) was added and the mixture was heated under reflux for 42 h. Addition of aqueous sodium hydroxide (10%; 100 ml) followed by isolation with chloroform gave crude bis-(2-hydroxycyclo-octyl) disulphide (7·2 g) as a glassy solid.

A solution of the disulphide in dry ether (25 ml) was added dropwise with stirring to lithium aluminium hydride (3·6 g, 0·095 mol) in ether (125 ml). The mixture was heated under reflux for 3 h and kept at 20° for 16 h. Water (7·2 g) was added dropwise and the product isolated with ether in the usual way. Distillation gave 2-*mercaptocyclo-octanol*, b.p. 101° at 0·7 mmHg (2·8 g) (Found: C, 60·1; H, 9·95; S, 20·25. $C_8H_{16}OS$ requires C, 60·0; H, 10·05; S, 19·95%), τ 6·4—6·8 (1H, m, 1-H), 6·9—7·4 (1H, m, 2-H), 7·3 (1H, s, OH), and 7·6—8·8 (13H, m, SH and methylenes).

10-*Phenyl*-9-*oxa*-11-*thiabicyclo*[6.3.0]*undecane.*— 2-Mercaptocyclo-octanol (1·49 g) and benzaldehyde (0·99 g) were treated as before with toluene-*p*-sulphonic acid (3·5 mg) in benzene (35 ml) (Dean–Stark apparatus; 1 h). The oily product (2·34 g) was recrystallised from light petroleum at −78° to give the *oxathiolan* (1·5 g), m.p. 47—48° (Found: C, 72·55; H, 7·75; S, 12·75. $C_{15}H_{20}OS$ requires C, 72·55; H, 8·1; S, 12·9%), τ 2·5—2·9 (5H, m, Ph), 4·0 and 4·1 (1H, two s, 10-H), 5·9—6·75 (2H, m, 1- and 2-H), and 7·6—9·5 (12H, m, methylenes). The two peaks at τ 4·0 (small) and 4·1 (large) were ascribed to the benzylic protons of the two diastereoisomers. In a later preparation oxathiolan containing roughly equal amounts of the two diastereoisomers was obtained.

trans-2-*Mercaptocyclo-oct-5-en*-1-*ol.*—9-Oxabicyclo[6.1.0]-non-4-ene [11] (12·4 g, 0·1 mol) was treated with sulphurated borohydride [from sulphur (19·2 g, 0·6 mol) and sodium borohydride (7·6 g, 0·2 mol) in THF (160 ml)] as described for *trans*-2-mercaptocyclo-octanol. The crude disulphide (8 g) was reduced with lithium aluminium hydride (4·0 g) in ether (100 ml) to give, after isolation with ether, the *mercapto-alcohol* (5·4 g, 35%), b.p. 92° at 1 mmHg (Found: C, 60·5; H, 8·9; S, 20·5. $C_8H_{14}OS$ requires C, 60·7; H, 8·9; S, 20·3%), τ 4·2—4·7 (2H, m, olefinic), 6·4—6·62 (1H, m, 1-H), 6·7—7·1 (1H, m, 2-H), 7·28 (1H, s, OH), 7·2—8·7 (8H, m, methylenes), and 8·55 (1H, d, *J* 10 Hz, SH).

This unsaturated mercapto-alcohol was very unstable and rapidly polymerised. In subsequent preparations it was not distilled, but purified by extraction into aqueous sodium hydroxide followed by acidification and isolation with ether. The material was then immediately converted into oxathiolan. In these later preparations only 1 mol. equiv. of sulphurated borohydride was used per mol. of epoxide and the reflux period was reduced to 1 h. In this way the yield of mercapto-alcohol based on epoxide was raised to 50%.

10-*Phenyl*-9-*oxa*-11-*thia*-trans-*bicyclo*[6.3.0]*undec*-4-*ene* — *trans*-2-Mercaptocyclo-oct-5-en-1-ol (25 g, 0·12 mol), benzaldehyde (17 g, 0·16 mol), toluene-*p*-sulphonic acid (18 mg), and hydroquinone (250 mg) were heated under reflux in benzene (250 ml) (Dean–Stark trap; 4 h). Isolation gave a solid (36·4 g, 94%), which was recrystallised from light petroleum to give the *oxathiolan*, m.p. 60—77° (Found: C, 73·35; H, 7·55; S, 13·1. $C_{15}H_{18}OS$ requires C, 73·15; H, 7·35; S, 13·0%), τ 2·4—2·8 (5H, m, Ph), 3·87 (0·4H, s, 10-H), 4·0 (0·6H, s, 10-H), 5·7—6·5 (2H, m, 1- and 8-H), and 7·5—8·7 (8H, m, methylenes), as a mixture of the two possible diastereoisomers.

2,4,5-*Triphenyl*-1,3-*oxathiolan.*— *erythro*-1,2-Diphenyl-2-mercaptoethanol (3·2 g; obtained from *trans*-stilbene oxide *via* reaction with sulphurated borohydride [6]) was condensed with benzaldehyde in benzene in the presence of toluene-*p*-sulphonic acid (6 mg). Crystallisation of the crude product from light petroleum (b.p. 60—80°) gave the *oxathiolan* (V) (3·25 g), m.p. 103—104° (Found: C, 79·0; H, 5·65; S, 9·8. $C_{21}H_{18}OS$ requires C, 79·2; H, 5·7; S, 10·05%), τ 2·25—2·8 (5H, m, 2-Ph), 3·0 (5H, s) and 3·05 (5H, s) (4- and 5-Ph), 3·7 (1H, s, 2-H), 4·7 (1H, d, *J* 6 Hz, 5-H), and 5·25 (1H, d, *J* 6 Hz, 4-H). Apparently only one diastereoisomer is produced; this is tentatively considered to be that in which the 2-phenyl group is *trans* to the 4- and 5-phenyl groups.

4,4,5,5-*Tetramethyl*-2-*phenyl*-1,3-*oxathiolan.*— Tetramethylethylene oxide was converted into 3-mercapto-2,3-dimethylbutan-2-ol by treatment with sulphurated borohydride in tetrahydrofuran followed by lithium aluminium hydride in the usual way. A portion (300 mg) which had been purified by base extraction was condensed with benzaldehyde (0·4 g) in benzene (10 ml) containing a trace of toluene-*p*-sulphonic acid (Dean–Stark). Isolation followed by chromatography on silica gel (elution with ether–light petroleum, 1 : 10) gave the *oxathiolan* (300 mg) as an oil (Found: C, 70·1; H, 7·95; S, 14·6. $C_{13}H_{18}OS$ requires C, 70·25; H, 8·15; S, 14·4%), τ 2·4—2·8 (5H, m, Ph), 3·92 (1H, s, 2-H), and 8·5, 8·54, 8·61, and 8·66 (each 3H, s, Me).

General Procedure for Reaction of Oxathiolans with Lithium Dialkylamides.—A flask fitted with a serum cap and magnetic stirrer was flushed with dry nitrogen; a slow stream

[9] C. Djerassi, M. Gorman, F. X. Markley, and E. B. Oldenburg, *J. Amer. Chem. Soc.*, 1955, **77**, 568.

[10] A. C. Cope, S. W. Fenton, and C. F. Spencer, *J. Amer. Chem. Soc.*, 1952, **74**, 5884.

[11] A. C. Cope, B. S. Fisher, W. Funke, J. M. McIntosh, and M. A. McKervey, *J. Org. Chem.*, 1969, **34**, 2231.

of gas was maintained throughout the reaction. n-Butyl-lithium in hexane (10—15% w/v) was transferred to the flask with a syringe followed by an excess of the secondary amine in ether (with cooling). After stirring for 10 min, a solution of the oxathiolan in ether was added. The mixture was worked up by pouring into an excess of aqueous potassium hydroxide. The ethereal layer was washed with aqueous sulphuric acid to remove amine, and after washing, drying, *etc.* gave the neutral fraction of the product. Acidification of the alkaline phase followed by isolation of the material liberated with ether gave the acidic fraction of the product. All operations were performed at 20°.

Reaction of 2-*Phenyl*-1,3-*oxathiolan with Lithium Diethylamide*.—The oxathiolan (5 g, 0·059 mol) in ether (50 ml) was added to lithium diethylamide [from n-butyl-lithium (0·059 mol) and diethylamine (6·6 g, 0·0905 mol)] according to the general procedure. The reaction time was 15 min. No material was obtained in the acidic fraction. The neutral fraction (8 g) was obtained as a brown oil; unchanged oxathiolan was not detected by i.r. or t.l.c. Distillation of a portion gave *NN*-diethylbenzamide, b.p. 84° at 0·1 mmHg (Found: C, 74·35; H, 8·25; N, 7·85. Calc. for $C_{11}H_{15}NO$: C, 74·55; H, 8·55; N, 7·9%), τ 2·75 (5H, s, Ph), 6·7 (4H, q, *J* 7 Hz, CH_2), and 8·9 (6H, t, *J* 7 Hz, CH_3).

Reaction of 2-*Phenyl*-1,3-*oxathiolan with Lithium* N-*Cyclohexyl*-N-*isopropylamide*.—The oxathiolan (5 g, 0·03 mol) in ether (50 ml) was treated with the amide from *N*-isopropylcyclohexylamine (10·8 g, 0·077 mol) and n-butyl-lithium (0·059 mol) according to the general procedure (15 min). The acidic fraction (2·5 g, 60%) was thiobenzoic acid, identified by comparison of its i.r. spectrum with that of an authentic sample. The neutral fraction (1·2 g), b.p. 162—167° at 0·3 mmHg, contained some *N*-cyclohexyl-*N*-isopropylbenzamide (i.r. and n.m.r.) but also showed considerable absorption in the aromatic region (n.m.r.) owing to contaminants.

Reaction of 2,5-*Diphenyl*-1,3-*oxathiolan with Lithium Dialkylamides* (*Spectroscopic Procedure*).—The reaction was carried out on a small scale by treating n-butyl-lithium solution (10%; 0·25 ml, 0·00039 mol) and the dialkylamine (0·00077 mol) in ether (2 ml) with the appropriate amount of oxathiolan. After work-up as before the ethereal and aqueous alkaline layers were transferred quantitatively to separate volumetric flasks and made up to known volumes by addition of ether and water, respectively. For the ethereal layer the yield of styrene was determined by measurement of the u.v. absorbance at 247 nm. The following values for the molar extinction coefficients at 247 nm were used: oxathiolan, 940; styrene, 12,970; dialkylbenzamide, 1710. Potassium thiobenzoate in the alkaline phase was estimated on the basis of $\lambda_{max.}$ 280 nm (ε 5960). The results are in the Table.

Reaction of 10-*Phenyl*-9-*oxa*-11-*thiabicyclo*[6.3.0]*undecane with Lithium Cyclohexylisopropylamide*.—The reaction was carried out in the usual way with n-butyl-lithium solution (15%; 2·5 ml, 0·0059 mol), *N*-isopropylcyclohexylamine (1·2 g, 0·0085 mol), and oxathiolan (1·17 g, 0·00473 mol) in ether (30 ml) for 15 min. The alkaline extract was shown spectroscopically to contain thiobenzoate ion (45%). The neutral fraction (0·87 g) was a brown oil the i.r. spectrum of which was compatible with an equimolar ratio of *trans*-cyclo-octene and unchanged oxathiolan. Chromatography on alumina with light petroleum (b.p. 30—40°) as eluant followed by distillation gave *trans*-cyclo-octene (0·15 g, 29%), b.p. 50° at 30 mmHg identified by comparison with an authentic sample (i.r. and g.l.c.).

Reaction of 10-*Phenyl*-9-*oxa*-11-*thia*-trans-*bicyclo*[5.3.0]-*undec*-4-*ene with Lithium Diethylamide. Preparation of* cis,trans-*Cyclo-octa*-1,5-*diene*.—A solution of dry diethylamine (6·55 g, 0·09 mol) in ether (10 ml) was added to an ice-cooled, stirred solution of methyl-lithium in ether (1·34M; 65 ml). After 10 min a solution of oxathiolan (10 g, 0·034 mol) in ether (30 ml) was added. After a further 12 h at 20° water was added and the ethereal layer was isolated. The dried ($MgSO_4$) solution was evaporated at 0° and the residue was dissolved in light petroleum (b.p. 30—40°) and washed with a small volume of methanol to remove most of the diethylbenzamide. After drying ($CaCl_2$), the solution was chromatographed on neutral alumina. Elution with light petroleum (b.p. 30—40°) followed by evaporation at 0° gave *cis,trans*-cyclo-octa-1,5-diene (2·0 g, 45%), identified by its n.m.r. and i.r. spectra.[7] G.l.c. (triscyanoethoxypropane–$AgBF_4$) showed contamination by *ca.* 1% of the *cis,cis*-isomer.

Reaction of 2,4,5-*Triphenyl*-1,3-*oxathiolan with Lithium Cyclohexylisopropylamide*.—The reaction was carried out in the usual way with n-butyl-lithium solution (14%; 3·2 ml, 0·00693 mol), *N*-isopropylcyclohexylamine (1·47 g, 0·0104 mol), and oxathiolan (1 g, 0·00315 mol) in ether (20 ml). After 2 days at 20° (the apparatus was covered with aluminium foil to exclude light) water was added and the neutral fraction was isolated in the usual way. Chromatography on a short column of neutral alumina (elution with light petroleum–ether, 4 : 1) followed by evaporation gave a colourless oil (0·38 g). The n.m.r. spectrum was identical with that of an authentic specimen of *cis*-stilbene except for the presence of a small peak at τ 3·05 due to <5% of *trans*-stilbene.

Reaction of 4,4,5,5-*Tetramethyl*-2-*phenyl*-1,3-*oxathiolan with Lithium Diethylamide*.—The reaction was carried out in the usual way with n-butyl-lithium in hexane (2M; 1·5 ml), diethylamine (300 mg), and the oxathiolan (165 mg) in ether. After 16 h at 18° no residual oxathiolan was detected by t.l.c. and the ethereal layer was washed successively with aqueous acid and water. The cooled (0°) ethereal solution was treated with bromine in carbon tetrachloride until a permanent yellow colour remained. Evaporation to dryness followed by extraction of the residue with light petroleum left a brown gum. Evaporation of the extract gave a crystalline residue (160 mg) which, after recrystallisation from ether, afforded white needles identified as 2,3-dibromo-2,3-dimethylbutane by comparison (m.p.; i.r. and n.m.r. spectra) with an authentic specimen.

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