NOTES.

583. *Catalytic Hydrogenation of Unsaturated Sulphides and Sulphones.*

By L. Bateman and F. W. Shipley.

High-pressure hydrogenation of organic sulphides over heavy-metal oxides or sulphides has the disadvantage that extensive hydrogenolysis usually occurs at the high temperatures required. Although there are exceptions to this, *e.g.*, thiophen and allyl phenyl sulphide have been reduced without appreciable C–S bond fission at 150—250°/2000 lb. per sq. in. in the presence of rhenium heptasulphide,[1] the hydrogenolysis and the inability to measure hydrogen absorption quantitatively with small samples make it desirable to develop less vigorous and more precise low-pressure methods.

By means of palladium on charcoal or barium sulphate, thiophen and certain of its derivatives have been reduced [2] at room temperature at 20—25 lb. per sq. in. and the same catalyst (on charcoal) has been used for the reduction of 1-methylallyl phenyl sulphide [3] and allyl and phenyl propenyl sulphide [4] at room temperature and pressure. For a range of sulphides and some sulphones we find the following generalizations: (i) Simple acyclic allylic or vinylic sulphides absorb hydrogen less readily than related olefins, but do so

[1] Broadbent, Slaugh, and Jarvis, *J. Amer. Chem. Soc.*, 1954, **76**, 1519.
[2] Mozingo, Harris, Wolf, Hoffhine, Easton, and Folkers, *ibid.*, 1945, **67**, 2092.
[3] Cope, Morrison, and Field, *ibid.*, 1950, **72**, 66.
[4] Tarbell and McCall, *ibid.*, 1952, **74**, 48.

completely in about one hour. (ii) Substitution in the allyl unit greatly reduces the initial rate and also the extent of reaction. (iii) Heterocyclic unsaturated sulphides react more readily than their acyclic analogues, but the effect of substitution noted in (ii) also operates, markedly so for the tetra-substituted double bond in 2 : 3-dimethylthia*cyclo*hex-2-ene. (iv) Unsaturated sulphones react much more readily than the corresponding sulphides,[3,5] but increased alkyl-substitution at the double bond or adjacent to the

Hydrogenation on palladium–charcoal.

Compound	Remarks
Olefins.	
*cyclo*Hexene	Rapid; complete in 5—10 min.
1-Methyl-2-1′-methyl*cyclo*hexyl*cyclo*hexene	Complete in 15 hr.
Acyclic allyl and vinyl sulphides.	
CH_2:CH·CH_2·SBu^n	Complete in 1 hr.
CH_2:CH·CH_2·SPh	Somewhat variable; complete in 1—3 hr.
$(CH_2$:CH·$CH_2)_2S$	50% in 18 hr.; some hydrogenolysis to thiol
Me·$[CH_2]_5$·CH:CH·SMe	Complete in 2—3 hr.
Me·$[CH_2]_5$·CH:CH·SEt	Complete in 4 hr.
Acyclic monosubstituted allyl sulphides.	
CH_2:CH·CHMe·SBu^n	94% in 23 hr.
CHMe:CH·CH_2·SBu^n	Complete in 35—45 hr.
CHMe:CH·CH_2·SPh	75% in 2 days, 100% in 5 days (trace of thiol formed)
CHPh:CH·CH_2·SPh	Very slow; 35% in 4 days (thiol formed)
Disubstituted allyl sulphides.	
CHMe:CH·CHMe·SBu^n	33% in 48 hr. (thiol formed)
CHMe:CH·CHMe·SMe	30% in 18 hr. (thiol formed)
CHMe:CH·CHMe·SPh	25% in 20 hr. (thiol formed)
3-Methylthio*cyclo*hexene	40% in 24 hr.
3-*iso*Propylthio*cyclo*hexene	20% in 17 hr.
Heterocyclic sulphides.	
2 : 5-Dihydrothiophen	100% in 12 min.
Thia*cyclo*hex-2-ene	100% in 15 min.
Thia*cyclo*hex-3-ene	90% in 18 hr.
2 : 3-Dihydro-5-methyl-2-*iso*propylthiophen	100% in 35 min.
2 : 3-Dihydrothia*cyclo*hex-2-ene	Very slow; 98% in 10 days
Sulphones.	
$(CH_2$:CH·$CH_2)_2SO_2$	All rapid; 100% in 8—15 min.
CHPh:CH·CH_2·SO_2·Ph	
*cyclo*Hex-2-enyl methyl sulphone	
2 : 5-Dihydrothiophen 1 : 1-dioxide	
2 : 3-Dihydro-5-methyl-2-*iso*propylthiophen 1 : 1-dioxide	
CHMe:CH·CHMe·SO_2·Ph	90% in 15 min., 100% in 1 hr.
2 : 3-Dimethylthia*cyclo*hex-2-ene 1 : 1-dioxide	Much slower; 100% in 2—3 hr. (no thiol detected)
tert.-Butyl *cyclo*hex-2-enyl sulphone	Very slow; 100% in 9 days (thiol formed)
CHMe:CH·CHMe·SO_2·Bu^n	Very slow; 26% in 5 days (thiol formed)
Miscellaneous	
CH_2:CH·CH_2·SO·Ph	Very slow (PhSH formed)
Me·CH(SMe)·CH:CH·SMe	Very slow; complete in 10 days
N-(2-Methylthia*cyclo*hex-2-en-1-yl)toluene-*p*-sulphonylimide	2 mol. H_2 (*i.e.*, hydrogenolysis + hydrogenation) in 1 hr.

sulphone group is again deactivating, in some cases severely. (v) Concomitant hydrogenolysis with liberation of thiol inhibits hydrogenation; this " poisoning effect " can be partly offset by the addition of strong bases, but these also reduce the activity of the catalyst.

Since unsaturated and the corresponding saturated sulphides can generally be separated chromatographically, even partial reduction with the minimum of side reactions provides a useful procedure for analysis and identification.[6]

[5] Backer and Strating, *Rec. Trav. chim.*, 1937, **56**, 1069.
[6] Bateman, Glazebrook, and Moore, *J.*, 1958, 2846.

Experimental.—The palladium chloride–Norite catalyst was prepared by a standard method.[7] For each run, 3·0 g. of catalyst, containing 1·4 millimoles of palladium chloride, was hydrogenated in absolute ethanol (15 ml.), and the resulting palladium–charcoal was washed free from hydrochloric acid on a filter funnel, and again shaken with hydrogen in the hydrogenation vessel until no further absorption occurred. The unsaturated compound (*ca.* 10 millimoles) in absolute ethanol (5—10 ml.) was then added, and hydrogenation carried out at room temperature and atmospheric pressure under vigorous agitation. Results are tabulated.

BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, 48–56, TEWIN ROAD, WELWYN GARDEN CITY, HERTS. [*Received, December* 23*rd*, 1957.]

[7] *Org. Synth.*, **26**, 78 (Catalyst C).

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584. *An Exchange Reaction of Arenesulphenyl Chlorides with Organic Disulphides.*

By C. G. MOORE and M. PORTER.

ARENESULPHENYL CHLORIDES (I) have been shown to undergo an exchange reaction with disulphides (II) (R = aryl, aralkyl, alkyl) to give unsymmetrical disulphides (III) (reaction 1*a*):

$$\underset{\text{(I)}}{\text{ArSCl}} + \underset{\text{(II)}}{\text{RS·SR}} \underset{b}{\overset{a}{\rightleftharpoons}} \underset{\text{(III)}}{\text{ArS·SR}} + \underset{\text{(IV)}}{\text{RSCl}} \quad \ldots\ldots\ldots\ldots (1)$$

Reaction occurs readily at room temperature in acetic acid solution, the product (III) often crystallising after a few days (see Table), but is slower in less polar solvents (ether, carbon tetrachloride, xylene). Experiments were confined to chlorides (I) in which Ar = 2 : 4-dinitrophenyl or 4-carboxy-2-nitrophenyl, but the reaction is likely to be general. An equilibrium (1*a* $\rightleftharpoons$ 1*b*) probably exists in a homogeneous system and this is supported by the facts that: (i) under anhydrous conditions, where competitive hydrolysis of the sulphenyl halides (I) and (IV) is absent, the reactants (I) and (II) were still present after long reaction periods; and (ii) quantitative yields of the product (III) [the stoicheiometric completion of (1*a*) being assumed] were not obtained. While the chloride (IV) was not identified it was shown that negligible loss of the sulphenyl halide group occurred under anhydrous conditions.

Reactions (2) and (3) should, in principle, compete with (1*a*, *b*), (2) giving the symmetrical diaryl disulphide (V). No evidence was obtained for reaction (2) when the chloride (I; Ar = 2 : 4-dinitrophenyl) was used in 100% excess over the disulphide (II; R = CH_2Ph). Similarly, interaction of this chloride with the unsymmetrical

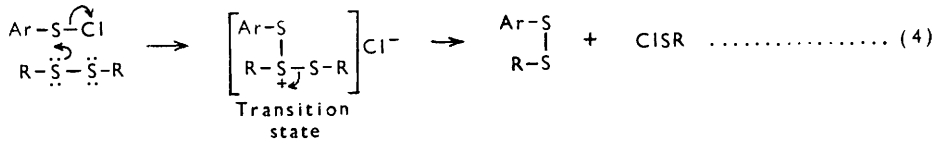
$$\underset{\text{(I)}}{\text{ArSCl}} + \underset{\text{(III)}}{\text{RS·SAr}} \rightleftharpoons \underset{\text{(V)}}{\text{ArS·SAr}} + \underset{\text{(IV)}}{\text{RSCl}} \quad \ldots\ldots\ldots (2)$$

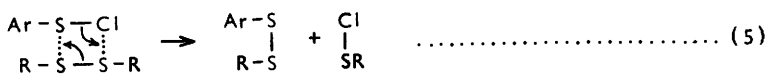
$$\underset{\text{(I)}}{\text{ArSCl}} + \underset{\text{(III)}}{\text{RS·SAr}} \rightleftharpoons \underset{\text{(III)}}{\text{ArS·SR}} + \underset{\text{(I)}}{\text{ArSCl}} \quad \ldots\ldots\ldots (3)$$

disulphides (III; Ar = 2 : 4-dinitrophenyl, R = CH_2Ph or *p*-tolyl) in anhydrous acetic acid failed to give any of the highly insoluble disulphide (V; Ar = 2 : 4-dinitrophenyl). Special effects must be operative, therefore, in these systems, leading to a specific orientation of S–S cleavage as in reaction (3), which perpetuates the production of the unsymmetrical compound.

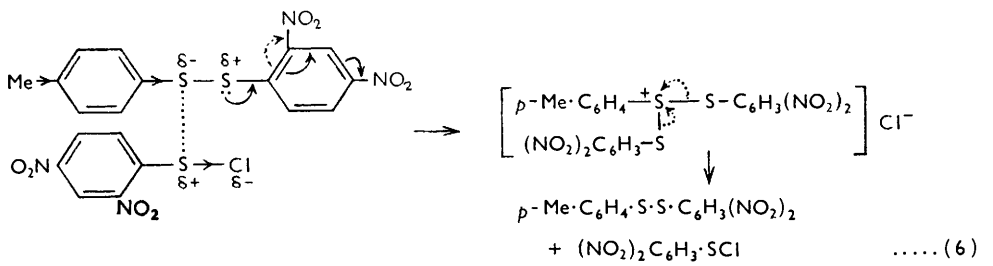
The present results, particularly the dependence of rate on the polarity of solvent, suggest that the exchange proceeds as in scheme (4), where considerable charge separation occurs in the transition state, rather than by a concerted process (5). The attacking agent is probably a polarised ArS–Cl molecule, as in (4), rather than the arenesulphenium

ion, $Ar{-}S^+$, since there is no evidence for ionisation in acetic acid solution of the arenesulphenyl chlorides studied in this work.[1] The non-occurrence of reaction (2*a*) in the systems now described is in agreement with the proposed mechanism, since electronic





factors would operate during the reaction of the unsymmetrical disulphide (III) with the sulphenyl halide (I) to favour heterolysis of the S–S bond in a preferred direction, leading to regeneration of the same disulphide (III) (reaction 3), *e.g.*, scheme 6.



The present reaction, as represented by scheme (4), bears a formal resemblance to the well-founded mechanism for the addition of sulphenyl halides to olefins,[2,3] and affords a further example of the infrequently observed heterolysis of S–S bonds by an *electrophilic* reagent.[4]

Experimental.—Materials. Unsymmetrical disulphides were prepared from the appropriate thiol and arenesulphenyl chloride in anhydrous ether [5] and recrystallised from ethanol, except for *4-carboxy-2-nitrophenyl phenyl disulphide* which was obtained as yellow needles (from carbon tetrachloride), m. p. 171·5—172·5° (Found: C, 50·5; H, 3·1; S, 20·7. $C_{13}H_9O_4NS_2$ equ ires C, 50·8; H, 3·0; S, 20·9%).

Reaction of arenesulphenyl chlorides with symmetrical disulphides. (1) In acetic acid. (i) The sulphenyl chloride [6,7] (1 millimole) and the disulphide (1 millimole) in " Reagent-grade " acetic acid (10 ml.) were kept at room temperature in the dark. The unsymmetrical disulphide usually separated out in 3—5 days and was freed from minor amounts of the hydrolysis products of the sulphenyl chloride [mainly the diaryl disulphide (V; Ar = 2 : 4-dinitrophenyl or 4-carboxy-2-nitrophenyl)] by extraction with hot ethanol and crystallisation from the same solvent. Examples are given in the Table. No diaryl disulphide (V) was formed when anhydrous acetic acid was used as solvent.

(ii) Reaction of the chloride (I; Ar = 2 : 4-dinitrophenyl) (2 mol.) with the disulphide (II; R = CH_2Ph) (1 mol.) in anhydrous acetic acid, as in (i) above, gave the product (III; Ar = 2 : 4-dinitrophenyl, R = CH_2Ph) but no product (V; Ar = 2 : 4-dinitrophenyl) even after 3 months. Similar results were obtained when using ether as solvent.

(iii) The disulphide (II; R = *p*-tolyl) (0·0025 mole) was dissolved in a 0·1M-solution (25·0 ml.) of the chloride (I; Ar = 2 : 4-dinitrophenyl) in anhydrous acetic acid, and reaction

[1] Kharasch, Buess, and King, *J. Amer. Chem. Soc.*, 1953, **75**, 6035, and references cited therein.
[2] Kharasch and Buess, *ibid.*, 1949, **71**, 2724.
[3] Orr and Kharasch, *ibid.*, 1956, **78**, 1201.
[4] Bateman, Moore, and Porter, *J.*, 1958, 2866, and references therein.
[5] Böhme and Stachel, *Z. analyt. Chem.*, 1956, **154**, 27.
[6] Kharasch, Gleason, and Buess, *J. Amer. Chem. Soc.*, 1950, **72**, 1796.
[7] Havlik and Kharasch, *ibid.*, 1955, **77**, 1150.

Reaction of arenesulphenyl chlorides (1 *mol.*) *with symmetrical disulphides* (1 *mol.*) *in acetic acid at* ca. 20°.

Reactants		Disulphide product, ArS·SR					
				Found (%) [g]			
Ar in ArSCl	R in RS·SR	Yield [a]	M. p.[f]	C	H	N	S
$(NO_2)_2C_6H_3$	Benzyl	68% in 3 days	111—112°	48·3	3·0	—	19·8, 20·0
			(111—112)	(48·4)	(3·1)	(8·7)	(19·9)
,, ...	Phenyl	*b*	84·2—85·2	46·8	2·9	—	20·9
			c	(46·8)	(2·6)	(9·1	(20·8)
,, ...	*p*-Tolyl	*d*	111—112	48·6	3·2	—	20·2
			(111—113)	(48·4)	(3·1)	(8·7)	(19·9)
$NO_2{\cdot}C_6H_3(CO_2H)$ ...	Phenyl	18% in 3 days	172—173	50·7	3·2	—	20·5
			(171·5—172·5)	(50·8)	(3·0)	(4·6)	(20·9)
,,	*n*-Butyl	25% in 5 days	128·5—130	46·0	4·8	4·5	22·4
			e	(46·0)	(4·6)	(4·9)	(22·3)

[a] These represent the amounts precipitated after the stated times and not the maximum yields obtainable. [b] Was not precipitated, but a yield of 16% was obtained by working up the reaction product. [c] Ref. 5 gives m. p. 86°. [d] Was not precipitated; 22% was obtained on working up after 7 days. [e] New compound. [f] Mixed m. p. in parentheses. [g] Calc. figures in parentheses.

was effected as in (i). Aliquot parts were withdrawn at intervals and the sulphenyl chloride contents determined iodometrically: [8]

Time (hr.)	0	16·5	23·0	42·5	138·0
Sulphenyl chloride remaining (%)	100	95·4	95·2	95·8	92·9

The solid obtained from the combined titrated solutions was recrystallised from ethanol, to give the disulphide (III; Ar = 2 : 4-dinitrophenyl, R = *p*-tolyl) (11%), m. p. 111—112°.

(2) In other solvents. (i) Reaction of the chloride (I; Ar = 2 : 4-dinitrophenyl) (1 millimole) with dibenzyl disulphide (1 millimole) in anhydrous ether (10 ml.) for 5 days at room temperature in the dark gave the product (III; Ar = 2 : 4-dinitrophenyl, R = CH_2Ph) (45%), m. p. 110·5—112° (Found: C, 48·5; H, 3·2; S, 19·9%). (ii) No unsymmetrical disulphide separated when a carbon tetrachloride solution of the same reactants as in (i) was kept for 14 days at room temperature; removal of the solvent at 30° and fractional crystallisation of the product gave unchanged reactants (II; R = CH_2Ph) and (III; Ar = 2 : 4-dinitrophenyl, R = CH_2Ph) (9%), m. p. 109—110·5° (Found: C, 48·6; H, 3·5; N, 8·7, 8·8%). (iii) The same disulphide (III) (27%) was obtained by heating the reactants in xylene on the steam-bath for 1 hr. (iv) No disulphide (III; Ar = 2 : 4-dinitrophenyl, R = *p*-tolyl) was isolated from a mixture of the chloride (I; Ar = 2 : 4-dinitrophenyl) (2·5 millimole) and di-*p*-tolyl disulphide (2·5 millimole) in anhydrous ether (50 ml.) after 18 days at room temperature. That insignificant reaction had occurred was confirmed by addition of aniline (5 millimole) in ether (5 ml.); the disulphide (II; R = *p*-tolyl) (2·45 millimole, 98%) was recovered and 2 : 4-dinitrobenzenesulphenanilide (0·75 millimole, 30%) was isolated; this had 141·5—143° (lit.,[9] m. p. 142·5—143°) (Found: C, 49·7; H, 3·3; S, 11·0. Calc. for $C_{12}H_9O_4N_3S$: C, 49·5; H, 3·1; S, 11·0%).

Action of the chloride (I; Ar = 2 : 4-*dinitrophenyl*) *on unsymmetrical disulphides.* When equimolar amounts of the sulphenyl chloride and the disulphide (III; Ar = 2 : 4-dinitrophenyl, R = CH_2Ph or *p*-tolyl) were dissolved in anhydrous acetic acid and the mixture was kept at room temperature none of the highly insoluble compound (V; Ar = 2 : 4-dinitrophenyl) separated, even after several months.

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[*Received, March 24th,* 1958.]

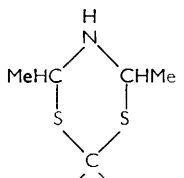
[8] Kharasch and Wald, *Analyt. Chem.*, 1955, **27**, 996.
[9] Billman, Garrison, Anderson, and Wolnak, *J. Amer. Chem. Soc.*, 1941, **63**, 1920.

585. *The Basicity of Dihydrothia-azetidines, Dihydrodithiazines, and Tetrahydrothiadiazines.*

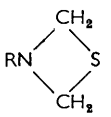
By D. J. Collins and J. Graymore.

Thialdine (I) is a very weak base, forming salts only with strong acids, these salts being extensively hydrolysed in aqueous solutions. The pK_a of thialdine was found, by the method of Bennett, Brooks, and Glasstone,[1] to be 2·85 at 25° in 30% aqueous ethanol.

The pK_a's of 3-*cyclo*hexyl-2 : 3-dihydro-1-thia-3-azetidine (II; R = C_6H_{11}), 5-*cyclo*hexyl-5 : 6-dihydro-1 : 3 : 5-dithiazine (III; R = C_6H_{11}), and the first pK_a of 3 : 5-di-*cyclo*hexyltetrahydro-1 : 3 : 5-thiadiazine, (IV; R = C_6H_{11}) were similarly found in 95% aqueous ethanol at 25° to be 2·6, 2·8, and 2·0 respectively. The pK_a of thialdine was also measured in 95% aqueous ethanol and found to be 2·7 at 25°. Change of solvent therefore appears to have little effect on the values obtained.



(I)



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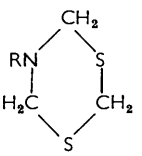
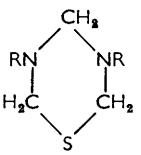


(III)



(IV)

The weak basicity of these compounds must presumably be attributed to inductive effects. There appears to be little experimental indication of the base-weakening effect of an α-sulphur substituent, probably owing to the ease with which compounds of this type undergo fission. In this connexion we found that the energy of activation for the quaternisation of diethylaminomethyl ethyl sulphide in nitrobenzene is 11,400 cal. mole^{-1}, which may be compared with that [2] (9700 cals. mole^{-1}) for the similar quaternisation of triethylamine.

The quaternisation of the cyclic bases with methyl iodide in nitrobenzene slowly proceeded to equilibria.

Plymouth and Devonport Technical College, Plymouth. [*Received, July 16th*, 1957.]

[1] Bennett, Brooks, and Glasstone, *J.*, 1935, 1821.
[2] Hinshelwood and Laidler, *J.*, 1938, 848.

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586. *Action of Organomagnesium Halides on Diaroyl Disulphides.*

By Mohamed A. Elkaschef and Michael H. Nosseir.

In their reaction with organomagnesium compounds diaryl disulphides were found by Wuyts [1] to behave as esters of hydrogen disulphide and undergo fission, RS·SR + R'·MgBr ⟶ RR'S + RS·MgBr, with final production of mixed sulphides and thiophenols. Disulphides were found by Schönberg *et al.*[2] to behave similarly towards phenyl-lithium. Gilman *et al.*[3] report that four mols. of phenylmagnesium bromide with one of ethyl thionbenzoate give benzophenone and two unidentified sulphur-containing compounds, or with one mol. of ethyl dithiobenzoate give a magnesium complex which, when treated with benzoyl chloride, gives triphenylmethyl thiobenzoate, proving that the phenyl group of the Grignard reagent adds to the carbon atom of the thiocarbonyl group and the MgBr to the sulphur, as is to be expected.

[1] Wuyts, *Bull. Soc. chim. France*, 1906, **35**, 166.
[2] Schönberg, Stephenson, Kaltschmitt, Petersen, and Schulten, *Ber.*, 1933, **66**, 237.
[3] Gilman, Robinson, and Beaber, *J. Amer. Chem. Soc.*, 1926, **48**, 2715.

Hepworth and Clapham,[4] using aryl- or alkyl-magnesium halides and ethyl thiobenzoate, thiocarbonate, and thioacetate, obtained tertiary alcohols and the thiol from which the thio-ester was derived. On the other hand, aroyl peroxides, which may be regarded as esters of hydrogen peroxide, were found by Gilman and Adams [5] to undergo fission, as in the case of disulphides, and in presence of phenylmagnesium bromide reaction goes further and affords triarylmethanol and phenol.

The present work concerns the action of arylmagnesium halides on diaroyl disulphides. When three mols. of phenylmagnesium bromide are added to one of dibenzoyl disulphide or of di-*p*-anisoyl disulphide and the magnesium complex is decomposed with sulphuric acid triphenylmethyl thiobenzoate and *p*-methoxyphenyldiphenylmethyl *p*-thioanisate respectively are obtained; when the decomposition is carried out with ammonium chloride the first disulphide gives triphenylmethanol and thiobenzoic acid, and the second gives phenyl *p*-thioanisate. *p*-Methoxyphenyl- or naphthyl-magnesium bromide with dibenzoyl disulphide gives respectively *p*-methoxyphenyl or naphthyl thiobenzoate, whichever method of decomposition is used. Use of six mols. of phenylmagnesium bromide and dibenzoyl disulphide affords triphenylmethanol, whilst two mols. give an unidentified unstable oil.

On decomposition of the magnesium complexes hydrogen sulphide was evolved. The odour of thiophenol was observed in almost all cases and thiophenol was proved to the present after decomposition of the complex leading to triphenylmethyl thiobenzoate.[6] These facts may explain the non-appearance of one of the sulphur atoms in the final products.

Experimental.—Action of phenylmagnesium bromide on dibenzoyl disulphide. (a) *3 mols. of bromide and 1 of disulphide.* (i) A Grignard solution from magnesium (0·72 g.), bromobenzene (3·2 c.c.), and ether (40 c.c.) was cooled to 0° and added to an ice-cold solution of dibenzoyl disulphide (2·74 g.) in benzene (70 c.c.). The mixture was refluxed for 2 hr., then kept overnight and poured into water (150 c.c.), ice (100 g.), and concentrated sulphuric acid (2·5 c.c.). Hydrogen sulphide was evolved and the smell of thiophenol was prominent. The organic layer was separated, the aqueous layer was extracted with ether, and the organic liquids were united, washed with water, dried (Na_2SO_4), and evaporated. The resultant oil crystallised on addition of light petroleum (b. p. 60—90°) and cooling. The solid triphenylmethyl thiobenzoate, recrystallised from light petroleum (b. p. 100—120°), had m. p. and mixed m. p. (cf. ref. 3) 188° and gave an orange colour in concentrated sulphuric acid (Found: C, 81·9; H, 5·2; S, 8·2. Calc. for $C_{26}H_{20}O_2S$: C, 82·1; H, 5·3; S, 8·4%).

To triphenylmethyl thiobenzoate (0·4 g.) in boiling acetic acid (20 c.c.) containing 1 c.c. of concentrated hydrochloric acid, zinc powder (activated with copper sulphate) (0·7 g.) was added, and the whole was refluxed for 6 hr. After cooling, the mixture was poured into water. Isolation with ether afforded triphenylmethane, m. p. and mixed m. p. (cf. ref. 7) 91°, and benzoic acid, m. p. and mixed m. p. 121°.

(ii) After a similar reaction the mixture was decomposed with ammonium chloride solution and ice. The organic layers yielded triphenylmethanol (1·2 g.), m. p. and mixed m. p. (cf. ref. 8) 163° from light petroleum (b. p. 60—90°). The aqueous layer on acidification gave thiobenzoic acid.

(b) *Six mols. of bromide and one of disulphide.* In reaction as above, with decomposition by acid, dibenzoyl disulphide (2·74 g.) and a Grignard reagent from bromobenzene (6·4 c.c.) gave triphenylmethanol (1·2 g.), m. p. and mixed m. p. 163°.

(c) *Two mols. of bromide and one of disulphide.* This reaction gave an unidentified red oil that decomposed spontaneously with evolution of hydrogen sulphide.

Action of p-*methoxyphenylmagnesium bromide* (3 *mols.*) *on dibenzoyl disulphide* (1 *mol.*). Dibenzoyl disulphide (2·7 g.) and a Grignard reagent from *p*-bromoanisole (5·6 g.), in a reaction as above, with refluxing for 3·5 hr. and decomposition with either sulphuric acid or ammonium

[4] Hepworth and Clapham, *J.*, 1921, **119**, 188.
[5] Gilman and Adams, *J. Amer. Chem. Soc.*, 1926, **47**, 2816.
[6] Rheinbolt's test for thiophenol, *Ber.*, 1927, **60**, 184.
[7] Gomberg, *Ber.*, 1903, **36**, 383.
[8] Acree, *Ber.*, 1904, **37**, 2755.

chloride, gave p-*methoxyphenyl thiobenzoate* from the organic layers as an oil which solidified under ethanol and, recrystallised therefrom (yield, 1·5 g.), had m. p. 102° and dissolved in concentrated sulphuric acid with a greenish yellow colour (Found: C, 68·7; H, 4·9; S, 13·0. $C_{14}H_{12}O_2S$ requires C, 68·8; H, 4·9; S, 13·1%).

Action of α-naphthylmagnesium bromide (3 *mols.*) *on dibenzoyl disulphide* (1 *mol.*). This reaction, with 3 hours' boiling and decomposition by either method, gave α-naphthyl thiobenzoate, m. p. 119° (cf. ref. 9) (from light petroleum), giving a green colour in sulphuric acid (Found: C, 77·1; H, 4·8; S, 11·8. Calc. for $C_{17}H_{12}OS$: C, 77·2; H, 4·5; S, 12·1%).

Action of phenylmagnesium bromide (3 *mols.*) *on di*-p-*anisoyl disulphide* (1 *mol.*). (i) Phenylmagnesium bromide (from 3·2 c.c. of bromobenzene) and di-*p*-anisoyl disulphide (3·3 g.), in a reaction as above, with refluxing for 5·5 hr. and decomposition with acid, gave p-*methoxyphenyldiphenylmethyl* p-*thioanisate* (2·8 g.), m. p. 178° [from light petroleum (b. p. 100—120°)], giving an orange solution in sulphuric acid (Found: C, 76·6; H, 5·4; S, 7·1. $C_{28}H_{24}O_3S$ requires C, 76·3; H, 5·4; S, 7·3%).

Reduction of this product as above gave *p*-anisic acid, m. p. and mixed m. p. 184°.

Boiling the ester for 1 hr. in ethanol containing concentrated hydrochloric acid (100 : 15 parts by vol.) gave *p*-anisic acid, m. p. 184°, and *p*-methoxyphenyldiphenylmethanol, m. p. and mixed m. p. (cf. ref. 10) 84° (from light petroleum–ether).

(ii) Reaction as above, but decomposition with ammonium chloride and ice, gave *phenyl* p-*thioanisate*, m. p. 99° [from light petroleum (b. p. 60—90°)] (yield 0·8 g.) (Found: C, 69·1; H, 4·9; S, 13·0. $C_{14}H_{12}O_2S$ requires C, 68·8; H, 4·9; S, 13·0%).

The same ester was obtained (m. p. and mixed m. p. 99°) by refluxing equimolecular amounts of *p*-anisoyl chloride with thiophenol.

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[*Received, September* 16*th*, 1957.]

[9] Taboury, *Compt. rend.*, 1904, **138**, 983.
[10] Kovache, *Ann. Chim.* (*France*), 1918, **10**, 200.

587. *Back-co-ordination from Oxygen to Boron in Organoboron Compounds.*

By E. W. ABEL, W. GERRARD, M. F. LAPPERT, and R. SHAFFERMAN.

SOME interest attaches to co-ordination at a tervalent boron atom in organoboron compounds; for it is hoped that intramolecular or intermolecular co-ordination might be harnessed, not only to eliminate ease of hydrolysis or of oxidation, but also to encourage cross-linking in the development of polymers.

In an investigation into factors influencing the co-ordination of amines to boron attached to oxygen, the base was added to the boron compound in a solvent. When there was no precipitate, heat of mixing indicated association, whereas a precipitated complex is described as stable if it remained after being for several hours at 20°/20 mm., and as unstable if under these conditions dissociation occurred. Results are recorded in Table 1.

In the trialkyl borates, back-co-ordination from three atoms of oxygen satisfies acceptor properties of boron, and repels outside donor molecules. Even when R = $CCl_3{\cdot}CH_2$, the inductive effect of nine atoms of chlorine does not reduce back-co-ordination sufficiently (possible *F*-strain being ignored), although the effect of nine atoms of fluorine does so. When R = Ph in any of the esters, back-co-ordination is very effectively compensated, presumably by an *M*-effect, although even then for the borates, complex formation can be hindered by *F*-strain due to *ortho*- or di-*ortho*-substitution in the ring. Phenyl attached to boron, as in the esters, $Ph{\cdot}B(OR)_2$, compensates back-co-ordination from two atoms of oxygen, by a mechanism which is not clear unless polarisability of phenyl allows co-ordination to occur. Results for the esters of diphenylboronous acid are in accordance with these comments. When *n*-butyl, instead of phenyl, is attached to boron [$BuB(OR)_2$], back-co-ordination from two atoms of oxygen is sufficient to impede

complex-formation with an external base, the $+I$-effect of the alkyl group attached to boron being insufficient itself to impede complex formation, as is clear from the fact that when two butyl groups are directly attached to boron [$Bu_2B{\cdot}OR$], evidence of complex-formation is found.

When the chain of the alkoxyl group is lengthened, Me to Et to Bu^n, decrease in stability of the corresponding complex is noticeable.

Table 2 gives results for a number of other nitrogen donor molecules, to show that overlying the factors mentioned there are steric factors related to the base which shift the stability of the complexes in one direction without altering the relation discussed.

TABLE 1. 1 : 1 *Complex formation with pyridine.*

R	$B(OR)_3$	$Ph{\cdot}B(OR)_2$	$Bu^n{\cdot}B(OR)_2$	$Ph_2B{\cdot}OR$	$Bu^n_2B{\cdot}OR$
Me	None [1]	Stable	Assocn.	Stable	Unstable
Et	—	Unstable	—	Stable	Assocn.
$CCl_3{\cdot}CH_2$	None [2]	Stable [2]	—	—	—
$CF_3{\cdot}CH_2$	Stable	—	—	Stable	Stable
Pr^n	—	—	—	Stable	—
Bu^n	None	—	None [2]	Assocn.	—
Ph	Stable	Stable [4]	Stable	Stable	Stable
$2\text{-}C_6H_4Y$	Unstable [3]	—	—	—	—
$2 : 6\text{-}C_6H_4Y_2$	None [3]	—	—	—	—

Y = Me, MeO, or Cl. Y′ = NO_2 or I.

TABLE 2. *Boron ester–amine co-ordination.*

	NH_3	$Et{\cdot}NH_2$	Et_2NH	Et_3N
$B(OPh)_3$ [3]	Stable	Stable	Unstable	Assocn.
$Ph{\cdot}B(OBu^n)_2$	Stable [5]	Assocn.	No assocn.	No assocn.
$Bu^n{\cdot}B(OMe)_2$	Unstable	No assocn.	No assocn.	No assocn.
$Ph_2B{\cdot}OBu^n$	Stable	Unstable	Assocn.	No assocn.
$Bu^n_2B{\cdot}OMe$	Unstable	Unstable	No assocn.	No assocn.
$Bu^n_2B{\cdot}OEt$	Unstable	Assocn.	No assocn.	No assocn.

TABLE 3. *Characterisation of complexes.*

		Found (%)		Required (%)	
Complex	M. p.*	Amine	B	Amine	B
$B(O{\cdot}CH_2{\cdot}CF_3)_3,NC_5H_5$	48°	21·1	2·9	20·4	2·8
$Ph{\cdot}B(OMe)_2,NC_5H_5$	31	34·9	4·8	34·6	4·7
$Bu^n{\cdot}B(OPh)_2,NC_5H_5$	66—70	23·5	3·1	23·7	3·3
$Ph_2B{\cdot}OMe,NC_5H_5$	78—80	28·5	3·8	28·8	3·9
$Ph_2B{\cdot}OEt,NC_5H_5$	80—82	27·6	3·5	27·4	3·7
$Ph_2B{\cdot}OPr^n,NC_5H_5$	57	26·5	3·5	26·1	3·6
$Ph_2B{\cdot}O{\cdot}CH_2{\cdot}CF_3,NC_5H_5$ †	97	21·9	—	23·1	—
$Ph_2B{\cdot}OPh,NC_5H_5$	—	23·6	3·4	23·2	3·2
$Bu^n_2B{\cdot}O{\cdot}CH_2{\cdot}CF_3,NC_5H_5$	*ca.* 4	25·8	3·3	26·1	3·6
$Bu^n_2B{\cdot}OPh,NC_5H_5$	56—57	26·8	3·3	26·7	3·6
$Ph_2B{\cdot}OBu^n,NH_3$	71—74	6·3	4·1	6·5	4·3
$Ph_2B{\cdot}OBu^n,Et{\cdot}NH_2$	61—63	15·7	3·8	15·9	3·8

* In sealed tubes. † Found: C, 66·9; H, 5·2. $C_{19}H_{17}ONF_3B$ requires C, 66·5; H, 5·0%.

Experimental.—*Tris*-2 : 2 : 2-*trifluoroethyl borate* (70%), b. p. 43°/60 mm., n_D^{20} 1·297 (Found: C, 23·6; H, 2·6; B, 3·55. $C_6H_6O_3F_9B$ requires C, 23·4; H, 2·0; B, 3·52%), was obtained by slow addition of 2 : 2 : 2-trifluoroethanol (3 mols.) in *n*-pentane to boron trichloride (1 mol.) in *n*-pentane at −80°, hydrogen chloride and solvent being then removed at 20°/100 mm.

2 : 2 : 2-*Trifluoroethyl diphenylboronite* (73%), b. p. 90°/0·2 mm., n_D^{20} 1·5190, d_4^{20} 1·1706 (Found: C, 63·8; H, 4·6; B, 4·12. $C_{14}H_{12}OF_3B$ requires C, 63·9; H, 5·9; B, 4·10%), was similarly obtained by equimolar interaction of diphenylboron chloride [6] and the alcohol.

[1] Venkataramaraj Urs and Gould, *J. Amer. Chem. Soc.*, 1952, **74**, 2948.
[2] Brindley, Gerrard, and Lappert, *J.*, 1956, 1540.
[3] Colclough, Gerrard, and Lappert, *J.*, 1955, 907; 1956, 3006.
[4] Dandegaonker, Gerrard, and Lappert, *J.*, 1957, 2872.
[5] Letsinger and Skoog, *J. Amer. Chem. Soc.*, 1955, **77**, 2491.
[6] Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697.

References to the preparation of other esters are: phenylboronates, $Ph{\cdot}B(OR)_2$, R = Me,[4] Et,[7] Ph [4]; *n*-butylboronates, $Bu^n{\cdot}B(OR)_2$, R = Me, Ph [8]; diphenylboronites, $Ph_2B{\cdot}OR$,[9] and di-*n*-butylboronites, $Bu^n{}_2B{\cdot}OR$, R = Me,[8] Et,[8] $F_3C{\cdot}CH_2$,[8] Ph.[10]

Complexes isolated are listed in Table 3.

THE NORTHERN POLYTECHNIC,
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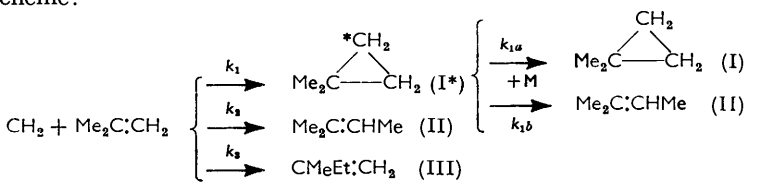
[*Received, February 20th*, 1958.]

[7] Brindley, Gerrard, and Lappert, *J.*, 1955, 2956.
[8] Gerrard, Lappert, and Shafferman, unpublished work.
[9] Abel, Gerrard, and Lappert, *J.*, 1957, 112.
[10] Gerrard, Lappert, and Shafferman, *J.*, 1957, 3828.

588. *Reactions of Methylene with* iso*Butene.*

By J. H. KNOX, A. F. TROTMAN-DICKENSON, and C. H. J. WELLS.

THE reactions of methylene with *iso*butene have been studied by photolysing keten in the presence of the olefin (ratio 1 : 2·8) in a Pyrex vessel with light from a medium-pressure mercury arc. The products were analysed by gas chromatography and identified by their infrared spectra. The formation of products may be interpreted in terms of the following scheme:



The variation of the yields of (I), (II), and (III) with pressure, shown in Fig. 1 for 20°, indicate that at pressures above about 4 cm. effectively all the (I*) molecules are deactivated by collision, *i.e.*, $k_{1a}[M] \gg k_{1b}$. At the higher pressures, therefore, the values of the relative yields give the ratios of the rate constants k_1, k_2, and k_3. The effect of temperature on the high-pressure ratios is shown in Fig. 2. The straight lines have the equations:

$$k_1/k_2 = 6{\cdot}0 \exp [+ 180 \text{ cal. mole}^{-1}/RT]$$
$$k_3/k_2 = 1{\cdot}2 \exp [+ 430 \text{ cal. mole}^{-1}/RT]$$

Addition to the double bond is several times more rapid than insertion into the C–H bonds. This is in agreement with Frey [1] who showed that for ethylene $k_1/k_2 = 1{\cdot}6$, after allowance for 4 ethylenic bonds in ethylene and only two in *iso*butene. Skell and Woodworth's results [2] on the reaction of methylene with *cis*-but-2-ene and Skell and Garner's [3] on the reactions of CBr_2 with olefins in general confirm the conclusion.

The small activation-energy differences are of the same order as those previously found for insertion of CH_2 into saturated hydrocarbons.[4] They likewise fall in an unexpected order in that $E_{CH_2} > E_{C=C} > E_{CH_3}$. However, their absolute values are probably low and are likely to be determined by steric requirements rather than by the strengths of the bonds broken or formed. The A factor ratios can be expressed in terms of the rates of attack on individual bonds as

$$A_{C=C} : A_{CH_2} : A_{CH_3} = 12 : 1{\cdot}00 : 0{\cdot}4$$

showing that the high reactivity of the double bond is due to a high entropy of activation, not to a low energy of activation. Skell and Woodworth's finding [2] that the

[1] Frey, *J. Amer. Chem. Soc.*, 1957, **79**, 1259.
[2] Skell and Woodworth, *ibid.*, 1956, **78**, 4496.
[3] Skell and Garner, *ibid.*, pp. 3409, 5431.
[4] Knox and Trotman-Dickenson, *Chem. and Ind.*, 1957, 731.

addition of CH_2 to *cis*-but-2-ene is stereospecific rules out the possibility that this high entropy is due to free rotation in the activated complex. Skell and Garner's results [3] on the reactions of CBr_2 show that its reactions are much more selective than those of methylene. Addition to *iso*butene is, for example, some 14 times as fast as the addition to hex-1-ene, whereas preliminary results with methylene indicate that its addition to *iso*butene and pent-1-ene occur at roughly the same rate.

At low pressures, as seen from Fig. 1, the ratios I/II and III/II fall as the pressure is reduced while (I + II)/III remains constant. Compounds (I) and (II) are, therefore, alternative final products, the latter being increasingly favoured at lower pressures. This is in full accord with the scheme outlined above, where activated 1 : 1-dimethyl*cyclo*propane

FIG. 1.

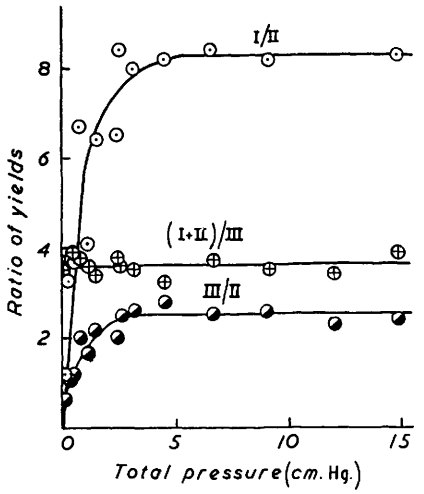
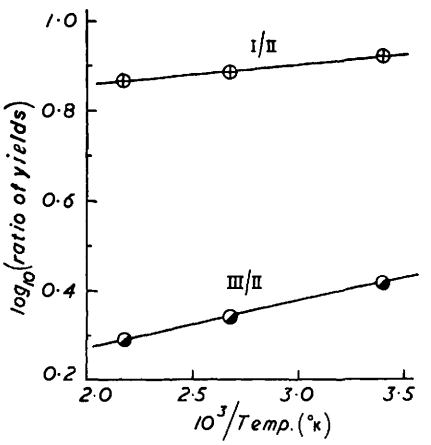


FIG. 2.



either isomerises [to (II)] or is stabilised by collision. The limiting pressure for stabilisation (about 4 cm.) may be compared with the corresponding pressure for activated *cyclo*propane [5] (about 200 cm.) and methyl*cyclo*propane [6] (about 40 cm.) formed by similar reactions of methylene with ethylene and propene. The larger number of degrees of freedom in the more complex activated molecules account for their greater lifetimes.

The isomerisation of (I*) might yield either 2-methylbut-2-ene (II) or 3-methylbut-1-ene (IV). Small quantities of the latter which has a boiling point close to that of the cyclic compound (I) might not have been detected on the chromatograms, and since the infrared identification was carried out with a sample from a high-pressure experiment, there is no direct analytical evidence that the but-1-ene was not formed at low pressures. However, the yield of (I + II) closely approaches zero at low pressures and so the percentage of the but-1-ene (IV) which could have been included in the analysis as dimethyl*cyclo*propane (I) must be low. Furthermore, the standard free-energy change (ΔF°) for the conversion of (II) into (IV) is $\Delta F^\circ = +3{\cdot}61$ kcal. mole^{-1} and if the isomerisation yields the methylbutenes (II) and (IV) in equilibrium proportions only $2{\cdot}4 \times 10^{-3}$ of the product will be the latter.

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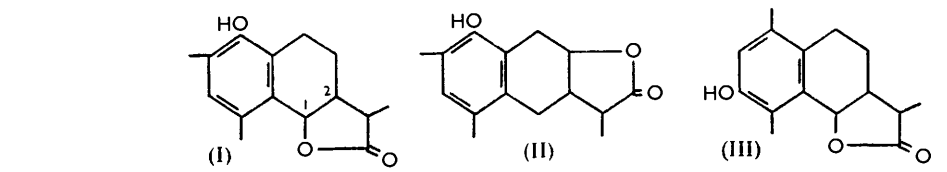
DEPARTMENT OF CHEMISTRY, UNIVERSITY OF EDINBURGH. [*Received, March 19th*, 1958.]

[5] Frey and Kistiakowsky, *J. Amer. Chem. Soc.*, 1957, **79**, 6373.
[6] Knox and Trotman-Dickenson, *Chem. and Ind.*, 1957, 1039.

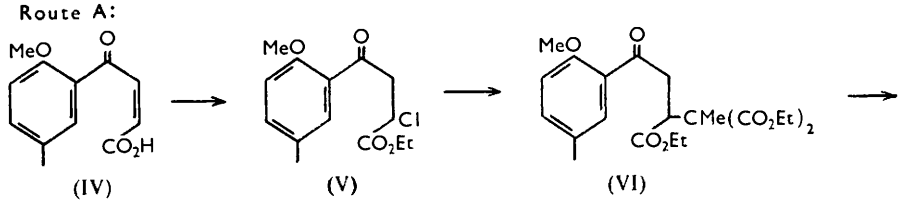
589. *Attempts to Synthesise* α-(1 : 2 : 3 : 4-*Tetrahydro*-1 : 5-*dihydroxy*-6 : 8-*dimethyl*-2-*naphthyl*)*propionic Lactone.*

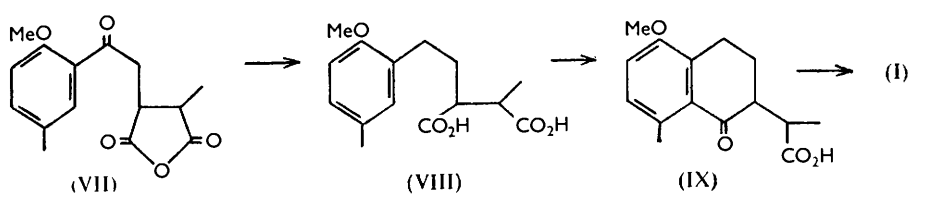
By Wesley Cocker, T. B. H. McMurry, (Mrs.) L. Mabrouk, and W. R. N. Williamson.

In attempts to synthesise the lactone (I), which at one time was considered to be desmotropo-ψ-santonin,[1] two reaction routes, shown below, were employed. Neither was successful, but a number of intermediates are now described. Since it is probable [2] that desmotropo-ψ-santonin has structure (II), other lines of approach to its synthesis are required.

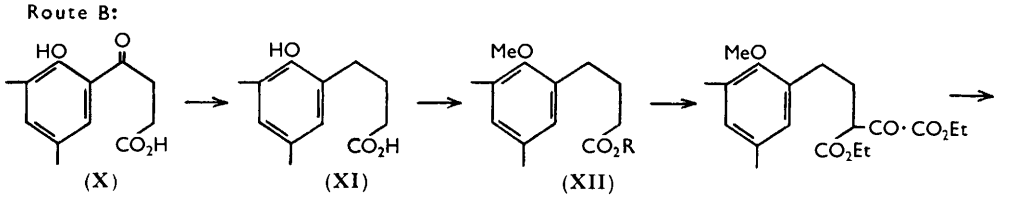


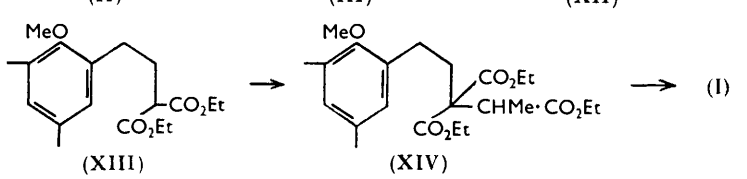
Route A:





Route B:





Route A is similar to that employed by Clemo, Haworth, and Walton [3] for the synthesis of desmotroposantonin (III). In our synthesis it was proposed to introduce the second nuclear methyl group in the final or penultimate stage. Yields of products in the earlier stages were disappointing and the method was abandoned.

In route B, β-(2-hydroxy-3 : 5-dimethylbenzoyl)propionic acid (X), previously prepared

[1] Cocker, Cross, and Lipman, *J.*, 1949, 939; cf. Clemo and Cocker, *J.*, 1946, 30.
[2] Chopra, Cocker, Edward, McMurry, and Stuart, *J.*, 1956, 1828.
[3] Clemo, Haworth, and Walton, *J.*, 1929, 2368; 1930, 1110.

in low yield by rearrangement of *m*-4-xylyl hydrogen succinate,[4] was produced in about 60% yield by condensation of *m*-4-xylenol with succinic anhydride in presence of aluminium chloride. The corresponding butyric acid (XI) was known,[4] and its methylation to (XII; R = H) which might have been expected to be difficult owing to hindrance was satisfactorily accomplished. Thereafter yields at each stage were disappointing, and the formation of the lactone (I) by this route is unprofitable.

Experimental.—Ultraviolet measurements were made on EtOH solutions.

Ethyl α-chloro-β-(2-methoxy-5-methylbenzoyl)propionate (V). β-(2-Methoxy-5-methylbenzoyl)acrylic acid [5] (IV) (7 g.) in absolute ethanol (60 c.c.) was saturated at 0° with hydrogen chloride; a copious white solid was deposited. After 12 hr. at 0° the solid *ester* (7 g.) was collected, washed with ice-cold ethanol, dried, and crystallised from ligroin (b. p. 80—100°) from which colourless needles, m. p. 78°, were deposited. It had $\lambda_{max.}$ 2500, 3200 Å (log ε 3·88, 3·58 respectively) (Found: C, 59·7; H, 6·2. $C_{14}H_{17}O_4Cl$ requires C, 59·1; H, 6·0%).

5-(2-Methoxy-5-methylphenyl)-5-oxopentane-2 : 3-dicarboxylic anhydride (VII). Diethyl methylmalonate (6·1 g.) was slowly added to a stirred suspension of powdered sodium (1 g.) in benzene (105 c.c.), and the stirred solution was then refluxed for 1·5 hr. The chloro-ester (V) (10 g.) in benzene (10 c.c.) was then slowly added with stirring to the cooled solution of sodio-derivative, and the mixture was refluxed for 3·5 hr. Water was added, the benzene layer was separated, and the aqueous layer was extracted twice with benzene. The combined benzene extracts were dried and the benzene was removed, leaving an oil (14·4 g.). A solution of the oil (5·7 g.) in methanol (60 c.c.) containing potassium hydroxide (12 g.) was refluxed for 2·25 hr., then diluted with water, and the methanol was removed by distillation. The residue, on acidification, afforded an oil which was heated at 160° for 1 hr., giving a resin (2·5 g.). This was triturated while still warm with light petroleum, giving the required *anhydride* (0·49 g.) which crystallised from benzene–light petroleum (b. p. 60—80°) as rhombs, m. p. 149° (Found: C, 65·2; H, 6·0. $C_{15}H_{16}O_5$ requires C, 65·2; H, 5·8%).

α-(2-Methoxy-5-methylphenethyl)-α'-methylsuccinic acid (VIII). A mixture of amalgamated zinc (10·5 g.), concentrated hydrochloric acid (10·5 c.c.), and the above anhydride (1·5 g.) was refluxed for 26 hr. On cooling, colourless needles (0·42 g.), m. p. 143—144°, were deposited, and extraction of the mother-liquor with benzene gave an acid (0·3 g.), m. p. 125—135°. Crystallisation of the latter from benzene gave the required *acid* as rhombs, m. p. 139°, $\lambda_{max.}$ 2790 Å (log ε 3·4) (Found: C, 64·6; H, 7·0. $C_{15}H_{20}O_5$ requires C, 64·3; H, 7·1%), which were undepressed by the acid of m. p. 143—144°. The acids are dimorphic modifications.

α-(1 : 2 : 3 : 4-Tetrahydro-5-methoxy-8-methyl-1-oxo-2-naphthyl)propionic acid (IX). The previous compound (1 g.) was heated in concentrated sulphuric acid (3 c.c.) at 65—70° for 10 min., then poured on crushed ice, and the solid (0·15 g.) was collected and washed with water. Two crystallisations from benzene gave the required *tetralone* (51 mg.) as prisms, m. p. 151—152°, $\lambda_{max.}$ 2600, 3080 Å (log ε 4·15, 3·2 respectively) (Found: C, 69·1; H, 6·6. $C_{15}H_{18}O_4$ requires C, 68·7; H, 6·9%).

β-(2-Hydroxy-3 : 5-dimethylbenzoyl)propionic acid [4] (X). Finely powdered aluminium chloride (129·5 g.) was stirred in ethylene dichloride (200 c.c.) cooled in an ice-bath, and succinic anhydride (59 g.) was gradually added. Stirring was continued at 0° for 0·5 hr., a clear solution being obtained. A cold solution of aluminium chloride (64·75 g.) in ethylene chloride (150 c.c.) containing 2 : 4-xylen-1-ol (61 g.) was then slowly added with stirring at 0° and the mixture was stirred for 22·5 hr., whilst the temperature gradually rose to that of the room. The dark red solution was poured into ice and hydrochloric acid, and the mixture was filtered, giving a solid (4·4 g.), m. p. 125—135°. The organic layer was then shaken with an equal volume of water, and the white slurry was filtered, giving a solid (55·7 g.), m. p. 144—147°. The combined solids were triturated with hot water to give the keto-acid (57 g.), m. p. 144—147° undepressed by a sample, m. p. 147—148°, prepared by the method of Cocker, Fateen, and Lipman.[4] A further quantity of the acid (11 g.; m. p. 144—147°) was obtained as follows. The ethylene dichloride–water filtrate was treated with sodium hydrogen carbonate and distilled in steam to remove solvent, and the residue acidified. The solid product was then crystallised from benzene (charcoal). The S-*benzylthiuronium salt* formed needles (from alcohol–water), m. p.

[4] Cocker, Fateen, and Lipman, *J.*, 1951, 929.

[5] Dave and Nargund, *J. Univ. Bombay*, 1938, **7**, 191; cf. "Organic Reactions," J. Wiley and Sons, New York, 1949, Vol. V, p. 286.

151° (Found: C, 61·0; H, 6·1. $C_{20}H_{24}O_4N_2S$ requires C, 61·8; H, 6·2%), and the *ethyl ester* needles (from ethanol), m. p. 67° (Found: C, 67·4; H, 7·3. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·2%).

γ-(2-Hydroxy-3 : 5-dimethylphenyl)butyric acid. This acid was prepared as described by Cocker, Fateen, and Lipman.[4] Its *methyl ester* formed needles (from light petroleum), m. p. 55° (Found: C, 69·8; H, 8·0. $C_{13}H_{18}O_3$ requires C, 70·2; H, 8·1%).

γ-(2-Methoxy-3 : 5-dimethylphenyl)butyric acid (XII; R = H). The hydroxy-acid [4] (XI) (50·2 g.), in a solution of sodium hydroxide (80 g.) in water (320 c.c.), was stirred whilst dimethyl sulphate (155 g.) was added during 0·75 hr. The mixture was refluxed and stirred for 2·5 hr., then cooled, and acidified. The precipitated red oil (51·3 g.) was collected in ether and distilled, the fraction (34 g.) of b. p. 175—180°/7 mm. being collected. This *acid* solidified (m. p. 37—41°) (Found: C, 69·7; H, 8·15. $C_{13}H_{18}O_3$ requires C, 70·2; H, 8·1%); it gave an *S-benzylthiuronium* salt, plates (from water), m. p. 127° (Found: C, 65·1; H, 7·2. $C_{21}H_{28}O_3N_2S$ requires C, 64·9; H, 7·3%), and an *ethyl ester* (XII; R = Et), b. p. 150°/8 mm. (Found: C, 71·9; H, 9·1. $C_{15}H_{22}O_3$ requires C, 72·0; H, 8·8%).

Diethyl 2-methoxy-3 : 5-dimethylphenethylmalonate (XIII). The above ester (XII; R = Et) (32·9 g.), in diethyl oxalate (38·4 g.) and benzene (50 c.c.), cooled to 0°, was slowly added to an ice-cold solution of sodium ethoxide (from sodium, 6 g.) in the minimum quantity of ethanol. After 18 hr. the pink solution was added to ice and hydrochloric acid, and the benzene layer was separated. The aqueous layer was exhaustively extracted with ether, the combined organic extracts were dried, and the solvents were removed. The remaining red oil (46 g.) was heated with powdered glass (50 g.) at 150—170° for 9 hr., then distilled, a fraction (26·7 g.) of b. p. 146—160°/7 mm. being collected. Several distillations failed to narrow the boiling range, but a fraction collected at 168°/4·5 mm. was used for analysis and was the required *ester* (XIII) (Found: C, 67·6; H, 8·5. $C_{18}H_{26}O_5$ requires C, 67·1; H, 8·1%). The *diamide* crystallised as needles (from methanol), m. p. 192—193° (Found: C, 63·8; H, 7·9; N, 11·1. $C_{14}H_{20}O_3N_2$ requires C, 63·6; H, 7·6; N, 10·6%).

Triethyl 5-(2-methoxy-3 : 5-dimethylphenyl)pentane-2 : 3 : 3-tricarboxylate (XIV). Potassium (0·97 g.) was dissolved in ethanol, and the solvent was then removed until a white flocculent precipitate appeared. The malonic ester (XIII) (8·6 g.) was then added with shaking and the remainder of the ethanol was removed, leaving a red jelly. Ethyl α-bromopropionate (5 c.c.) was then added slowly with shaking, and the mixture was heated at 100° for 3·5 hr., and kept at room temperature for 36 hr. The product was dissolved in ether and filtered to remove potassium bromide. Distillation of the ethereal extract gave a colourless oil (6·1 g.), b. p. 187—200°/6 mm. A specimen of the *tricarboxylic ester* collected for analysis had b. p. 200°/6 mm. (Found: C, 65·15; H, 8·3. $C_{23}H_{34}O_7$ requires C, 65·4; H, 8·1%).

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590. *Three Iodides of Rhenium.*

By R. D. PEACOCK, A. J. E. WELCH, and L. F. WILSON.

ALTHOUGH fluorides, chlorides, and bromides of rhenium are known, the existence of iodides has been disputed. The early claim of I. and W. Noddack that rhenium tetraiodide is formed from the elements on heating has not been substantiated,[1] and work in these laboratories shows that iodine does not combine with rhenium even at red heat. We have now successfully isolated rhenium tetraiodide by a method analogous to that used in making the corresponding osmium compound OsI_4 from osmic acid,[2] namely, the reduction of per-rhenic acid by hydriodic acid.

[1] Rulfs and Elving, *J. Amer. Chem. Soc.*, 1950, **72**, 3304.
[2] Cf. Sidgwick, "The Chemical Elements and their Compounds," Clarendon Press, Oxford, 1950, Vol. II, p. 1494.

Per-rhenic acid is acted on by cold hydriodic acid, iodine is released, and a dark brown solution is formed. Evaporation to dryness at room temperature yields black rhenium tetraiodide, which *X*-ray photographs show to be nearly non-crystalline. At an intermediate stage in the evaporation black plate-like crystals, presumably of hydrated iodorhenic acid H_2ReI_6,nH_2O, appear. The tetraiodide is very hygroscopic and dissolves easily in water to give a brown solution which, however, soon hydrolyses, depositing hydrated rhenium dioxide, ReO_2,nH_2O. It is also soluble in acetone and ether to give dark brown solutions.

Rhenium tetraiodide is unstable; it loses iodine in a vacuum at room temperature, and when heated rapidly decomposes. Weight losses during this thermal decomposition appear to indicate two solid iodide phases, the tri-iodide, ReI_3, and the monoiodide, ReI.

Rhenium tri-iodide is a black crystalline solid obtained by heating rhenium tetraiodide in a sealed tube to 350°. Alternatively, ammonium iodorhenate $(NH_4)_2ReI_6$ is decomposed in a vacuum at 325°, and the solid residue heated with excess of iodine in a sealed tube at 200°. In both instances the superfluous iodine is dissolved in carbon tetrachloride, which leaves the insoluble rhenium tri-iodide. The tri-iodide is only slightly soluble in water (cf. RuI_3) and dilute acids; it is nearly insoluble in alcohol, acetone, and ether. Like the tetraiodide, it loses iodine slowly in a vacuum, especially when warmed.

The phase formed when the tetraiodide is heated to constant weight at 110° in a stream of nitrogen containing a little iodine is rhenium monoiodide. *X*-Ray photographs show this to have a simple cubic unit cell, with a cell edge of 9·33 Å. It recombines with iodine at 200° in a sealed tube to form the tri-iodide; when heated alone in a vacuum the ultimate product is rhenium metal.

Experimental.—Rhenium tetraiodide. Rhenium metal powder (1 g.) was dissolved in dilute hydrogen peroxide (20 vol.). The colourless solution was evaporated nearly to dryness on a steam-bath several times to remove excess of hydrogen peroxide. 15 ml. of water were added, followed by a large excess of concentrated hydriodic acid which had been freshly distilled over red phosphorus. The solution was evaporated almost to dryness in a vacuum desiccator and was allowed to stand for 3 days in a desiccator over phosphorus pentoxide and solid sodium hydroxide. (The product loses iodine progressively under a vacuum.) The black amorphous residue was *rhenium tetraiodide* (Found: Re, 27·1; I, 73·4. ReI_4 requires Re, 26·8; I, 73·2%). Its infrared spectrum showed H_2O and −OH to be absent.

Rhenium tri-iodide. Rhenium tetraiodide (0·2 g.) was heated in a sealed tube at 350° for 6 hr. After the tube was cooled and opened, excess of iodine was removed from the product by washing with carbon tetrachloride, in which the *tri-iodide* is insoluble (Found: I, 67·7. ReI_3 requires I, 67·1%). Alternatively, ammonium iodorhenate(IV) (2 g.) was heated in a vacuum at 325° for several hr.; the cold residue, which consisted essentially of impure rhenium monoiodide, was heated with excess of iodine in a sealed tube at 200°. The product, which was a mixture of tri-iodide and iodine, was washed with carbon tetrachloride or water to remove the iodine (Found: Re, 33·2; I, 66·6. ReI_3 requires Re, 32·9; I, 67·1%).

Rhenium monoiodide. Rhenium tetraiodide (0·2 g.) was heated to 110° in a stream of nitrogen in the presence of a small vapour pressure (15 mm.) of iodine for 16 hr. The product was *rhenium monoiodide* (Found: Re, 60·2; I, 39·4. ReI requires Re 59·5; I, 40·5%).

Analysis.—Iodine. Portions (40 mg.) were suspended in 20 ml. of water, 10 mg. of manganese dioxide were added, and the whole boiled. 2N-Sulphuric acid was added dropwise until no more iodine was evolved. The iodine was collected in carbon tetrachloride and titrated against 0·01N-sodium thiosulphate.

Rhenium. This was estimated either spectrophotometrically by absorption of the α-furfuraldoxime complex measured at 532 μ [3] or as nitron per-rhenate after removal of iodide.

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[3] Meloche, Martin, and Webb, *Analyt. Chem.*, 1957, **29**, 527.

591. *Preparation of Cyanamide.*

By Alexander Lawson and J. O. Stevens.

As crystalline cyanamide is not available commercially in this country, it is usually prepared from calcium cyanamide by the method described in *Inorganic Syntheses* [1] or in *Organic Syntheses*.[2] Both procedures are time-consuming and tedious. For small laboratory preparations the following method, giving no less yield, is quick and more convenient.

Calcium cyanamide (16 g.) is ground with powdered oxalic acid dihydrate (24 g.) and stirred with ether (200 ml.) and water (10 ml.) for 30 min. Some heat is generated but not enough to cause the ether to boil. The suspension is filtered and the solid washed with ether (50 ml.). The ether solution is then shaken with " Biodeminrolit " de-ionising resin (10 g.) for a few minutes and set aside for 1 hr. This removes the small quantity of oxalic acid present. After filtration the ether solution is kept over anhydrous sodium sulphate for 30 min., then evaporated. The crystalline residue of cyanamide may be recrystallised from benzene–ether (yield 2·5—3·0 g.; m. p. 42—44°).

The method is equally applicable to sodium acid cyanamide which gives near quantitative yield.

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[1] *Inorg. Synth.*, 1950, **3**, 39.
[2] *Org. Synth.*, 1954, **34**, 67.

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592. o-*Hydroxybenzenesulphonamide.*

By C. A. Bartram, P. Oxley, D. A. Peak, and J. S. Nicholson.

Raffa [1] described *o*-hydroxybenzenesulphonamide, prepared *via* the diazonium salt of *o*-aminobenzenesulphonamide, as a strongly acidic substance of high melting point (decomposition above 330°) and low solubility in organic solvents. These properties appeared to us to be incompatible with the expected properties of *o*-hydroxybenzenesulphonamide. Chelation, which Raffa [2] invokes in order to explain the high acidity, would be expected to confer a melting point appreciably lower than those of the *m*- and *p*-isomers (165° and 174° respectively). Re-examination of Raffa's product has in fact shown that it is not *o*-hydroxybenzenesulphonamide but the isomeric *o*-aminobenzenesulphonic acid. This follows from the demonstration that the product contains a diazotisable amino-group and is confirmed by the synthesis of *o*-hydroxybenzenesulphonamide of the expected properties by an unambiguous route. To this end, several routes were tried. Demethylation of *o*-methoxybenzenesulphonamide gave unrecognisable products. Reaction of *o*-acetoxybenzenesulphonyl chloride with aqueous ammonia gave a compound, probably *o*-(*o*-hydroxybenzenesulphonyloxy)benzenesulphonamide, as sole product. Reductive elimination of the amino-group of 4-amino-2-hydroxybenzenesulphonamide [3] by diazotisation and hypophosphite reduction also failed. *o*-Hydroxybenzenesulphonamide was finally obtained from *o*-benzyloxyaniline by conversion *via* the diazonium salt into *o*-benzyloxybenzenesulphonyl chloride and thence into the sulphonamide, followed by catalytic debenzylation.

The recognition of Raffa's product as *o*-aminobenzenesulphonic acid provides a simple explanation of the high acidity of the various acyl derivatives,[2] these now being formulated

[1] Raffa, *Il Farm.* (*Ed. Sci.*), 1955, **10**, 532.
[2] *Idem, ibid.*, 1956, **11**, 46.
[3] Thorpe and Williams, *Biochem. J.*, 1941, **35**, 63.

as *o*-acylaminobenzenesulphonic acids. The formation [4] of tribromoaniline with bromine water becomes the normal reaction,[5] not requiring any Hofmann-like transposition as postulated by Raffa.

Experimental.—o-*Aminobenzenesulphonic acid.* Repetition of Raffa's preparation [1] afforded the product as plates, m. p. >320° (Found: N, 8·4. Calc. for $C_6H_7O_2NS$: N, 8·1%). It gave a highly acidic solution in water (pH *ca.* 1), and the solution after diazotisation gave a strongly positive coupling reaction with alkaline β-naphthol.

o-*Benzyloxybenzenesulphonamide.* The diazonium solution from *o*-benzyloxyaniline [6] (25·0 g.), concentrated hydrochloric acid (28 c.c.), acetic acid (28 c.c.), and sodium nitrite (9·55 g.) in water (30 c.c.) was added to a saturated solution of sulphur dioxide in acetic acid (90 c.c.) and benzene (90 c.c.) containing finely powdered cupric chloride dihydrate (6·0 g.). The mixture was stirred at 40° for 3 hr., cooled, and diluted with water, and crude *o*-benzyloxybenzenesulphonyl chloride isolated in benzene. After removal of benzene the residue was stirred with ammonia (60 c.c.; *d* 0·88) and water (60 c.c.) for 2 hr. and then at 100° for 30 min. o-*Benzyloxybenzenesulphonamide* was extracted from the crude product with 2N-sodium hydroxide (250 c.c.), filtered (charcoal), and acidified with dilute hydrochloric acid, and the precipitate (8·3 g.) recrystallised from aqueous methanol to give colourless needles, m. p. 129—131° (Found: C, 59·3; H, 4·9; N, 5·6. $C_{13}H_{13}O_3NS$ requires C, 59·3; H, 4·9; N, 5·3%).

Acetic anhydride in pyridine at room temperature gave N-*acetyl*-o-*benzyloxybenzenesulphonamide*, prisms (from methanol), m. p. 142—144° (Found: C, 59·1; H, 5·0; N, 4·5. $C_{15}H_{15}O_4NS$ requires C, 59·0; H, 4·9; N, 4·6%).

o-*Hydroxybenzenesulphonamide.* *o*-Benzyloxybenzenesulphonamide (3·15 g.) in acetic acid (150 c.c.) was shaken with hydrogen and 10% palladium–charcoal (1·5 g.) at room temperature. Absorption of hydrogen was complete in 3 min. The filtrate from the catalyst was evaporated to dryness *in vacuo* below 50° and the residue recrystallised from benzene (charcoal) to give o-*hydroxybenzenesulphonamide* (1·5 g.) as needles or plates, m. p. 139—141° [Found: C, 41·8; H, 4·1; N, 8·3; S, 17·9%; *M* (Rast), 172. $C_6H_7O_3NS$ requires C, 41·6; H, 4·05; N, 8·1; S, 18·5%; *M*, 173].

Acetic anhydride in pyridine at room temperature afforded o-*acetoxy*-N-*acetylbenzenesulphonamide*, plates (from benzene), m. p. 115—117·5° (Found: C, 47·3; H, 4·3; N, 5·6. $C_{10}H_{11}O_5NS$ requires C, 46·7; H, 4·3; N, 5·45%). Toluene-*p*-sulphonyl chloride in pyridine at 100° (15 min.) gave a *toluene*-p-*sulphonyl derivative*, colourless prisms (from methanol), m. p. 137—139° (Found: C, 47·3; H, 3·9; N, 4·5. $C_{13}H_{13}O_5NS$ requires C, 47·7; H, 4·0; N, 4·3%), probably the *O*-tosyl derivative since the product gave no colour with ferric chloride and was soluble in sodium hydroxide but not in sodium hydrogen carbonate solution. Bromine water in slight excess gave a *dibromo-compound* (90%), colourless needles (from water), m. p. 210—214° (Found: C, 22·4; H, 1·7; N, 3·9. $C_6H_5O_3NSBr_2$ requires C, 21·8; H, 1·5; N, 4·2%).

Reaction of o-*acetoxybenzenesulphonyl chloride with ammonia.* *o*-Acetoxybenzenesulphonyl chloride [7] (20 g.) was kept in 40% aqueous ammonia for 2 days. The filtered mixture was evaporated on the steam-bath, and the residue digested with water and again evaporated. The oily residual solid was boiled with dilute aqueous sodium hydroxide, and the cooled solution acidified with sulphuric acid. Recrystallisation from water afforded a *compound*, m. p. 157—159° (Found: C, 43·1; H, 3·3; N, 4·3; S, 19·0. $C_{12}H_{11}O_6NS_2$ requires C, 43·8; H, 3·3; N, 4·25; S, 19·4%).

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[4] Raffa, *Il Farm.* (*Ed. Sci.*), 1956, **11**, 62.
[5] Limpricht, *Annalen*, 1875, **177**, 79.
[6] Sieglitz and Koch, *Ber.*, 1925, **58**, 79.
[7] Anschütz, *Annalen*, 1918, **415**, 69.