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677. *Olefinic Additions with Asymmetric Reactants. Part IV.* The Addition of* (±)-, (+)-, *and* (−)-1-*Phenylpropane-2-thiol to Olefins. The Optical Stability of Asymmetric Sulphones.*

By C. L. Arcus and P. A. Hallgarten.

Free-radical and Michael additions of (±)-, (+)-, and (−)-1-phenylpropane-2-thiol to β-nitrostyrene are described, together with separations of the diastereoisomeric sulphides or the corresponding sulphones. Reactions of the (±)-thiol with *trans*-1 : 2-dibenzoylethylene and 4′-nitrochalkone have been investigated.

The steric course of addition is discussed. (−)-2 : 4-Dinitrophenyl α-methylphenethyl sulphone is optically stable in acetic acid at 100°.

For a further study of dissymmetric olefinic addition, it appeared that an asymmetric thiol would be of use, it being known that thiols add readily to olefins of suitable structure by both a free-radical and an anionic (Michael) mechanism. A method for the preparation of (±)-, (+)-, and (−)-1-phenylpropane-2-thiol has been described.[1] The addition of this thiol (I) to an olefin (III) leads potentially to the diastereoisomeric sulphides (VI) and (VII) and if asymmetry in the thiol (I) results in dissymmetric addition (partial asymmetric synthesis), the sulphides will be formed in unequal amounts. In the present work a number of such additions have been investigated.

β-*Nitrostyrene.*—Addition of (±)-1-phenylpropane-2-thiol to β-nitrostyrene, whether initiated by ascaridole (a free-radical reaction) or catalysed by piperidine, yielded two diastereoisomers, (±)-α-methylphenethyl 2-nitro-1-phenylethyl sulphide-A and -B, which were separated by fractional crystallisation and with hydrogen peroxide in acetic acid gave the corresponding sulphones, -A and -B.

Ascaridole-initiated addition of the (+)-thiol (90% optically pure) gave an oil from which solid sulphides could not be obtained; oxidation, and fractional crystallisation of the product, yielded a (−)-sulphone-A and impure (+)-sulphone-B. A similar procedure with optically pure (−)-phenylpropane-2-thiol gave the diastereoisomeric sulphides as an oil, and thence a (+)-sulphone-A and (−)-sulphone-B. These two sulphones were also obtained by oxidation of the sulphides from the piperidine-catalysed addition of the (−)-thiol.

Addition of (±)-, (+)-, *and* (−)-1-*Phenylpropane*-2-*thiol to* β-*Nitrostyrene.*

Thiol	Sulphide-A	Sulphone-A	Sulphide B	Sulphone B
(±)-	$d_{R}l_{\alpha} + l_{R}d_{\alpha}$ M. p. 76°	$d_{R}l_{\alpha} + l_{R}d_{\alpha}$ M. p. 117·5°	$d_{R}d_{\alpha} + l_{R}l_{\alpha}$ M. p. 53°	$d_{R}d_{\alpha} + l_{R}l_{\alpha}$ M. p. 111°
(+)-	—	$d_{R}l_{\alpha}$. M. p. 140° $[\alpha]^{17}$ −46·5°	—	$d_{R}d_{\alpha}$. M. p. 79—83° * $[\alpha]^{21}$ +74·5°
(−)-	—	$l_{R}d_{\alpha}$. M. p. 139·5° $[\alpha]^{21}$ +46·5°	—	$l_{R}l_{\alpha}$. M. p. 102·5° $[\alpha]^{20}$ −89·5°

* Sterically impure. [α] are for λ 5893 Å and acetone solutions.

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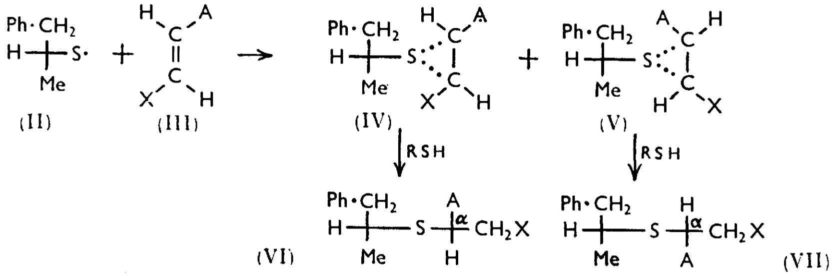
* Part III, *J.*, 1955, 34.

[1] Arcus and Hallgarten, *J.*, 1956, 2987.

The piperidine-catalysed addition of five sterically symmetrical arenethiols to β-nitrostyrene was found by Cason and Wanser[2] to yield in each instance a single product. The product from thiophenol was shown to be 2-nitro-1-phenylethyl phenyl sulphide, by reduction to the amine which was also formed by reaction of β-chlorophenethylamine with sodium thiophenoxide. It is concluded that the present sulphides are the diastereoisomers of analogous structure, as given above.

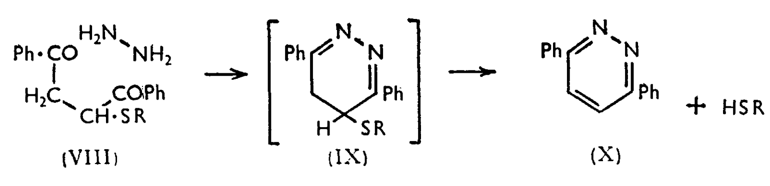
(+)- and (−)-1-Phenylpropane-2-thiol are assigned the arbitrary configurations d_R and l_R (R referring to the α-methylphenethyl radical); the new asymmetric centre which is present in the sulphides and sulphones is termed d_α or l_α [cf. (VI) and (VII)]. The rotations for the sulphones derived from the (−)-thiol, given in the Table, show that the new centre (α) contributes a (+)-rotation in the A- and a (−)-rotation in the B-sulphone; the assignments, l_Rd_α, etc., in the Table follow from this correlation and from the fact that a 1 : 1 mixture of (+)- and (−)-sulphone-A gave a (±)-sulphone of m. p. 117—118°.

$$\text{(I) } Ph{\cdot}CH_2{\cdot}CHMe{\cdot}SH + Q{\cdot} \longrightarrow Ph{\cdot}CH_2{\cdot}CHMe{\cdot}S{\cdot} \text{ (II)} + QH$$



Quantitative determination of ratios of diastereoisomers did not prove practicable, but in every instance a substantial amount of each diastereoisomer was isolated, and it is proved that neither the peroxide-initiated free-radical addition nor the base-catalysed Michael addition proceeds unilaterally to yield the new asymmetric centre in a single configuration.

trans-1 : 2-*Dibenzoylethylene.*—Reaction, initiated by ascaridole, of (±)-1-phenylpropane-2-thiol with *trans*-1 : 2-dibenzoylethylene gave a crystalline sulphide, $CH_2Ph{\cdot}CHMe{\cdot}S{\cdot}CH(COPh){\cdot}CH_2{\cdot}COPh$, m. p. 87·5°, together with an oil probably containing a diastereoisomer. The oil, on reaction with hydrazine, formed a sulphur-containing material which on purification yielded 3 : 6-diphenylpyridazine (X); it is probable that the sulphide (VIII) gave a dihydropyridazyl sulphide (IX) which by



elimination formed the diphenylpyridazine. The oil is therefore considered to have contained a dibenzoylethyl α-methylphenethyl sulphide, although no information on its configuration was obtained from its conversion into diphenylpyridazine.

The sulphides (crystalline solid, and oil) were oxidised by hydrogen peroxide in cold acetic acid to the same sulphone. In this instance the sulphone contains a carbonyl group adjacent to the second asymmetric centre, and conversion into the most stable diastereoisomer is possible by enolisation. It is probable that, in addition to the crystalline

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[2] Cason and Wanser, *J. Amer. Chem. Soc.*, 1951, **73**, 142.

isomer, a second diastereoisomeric sulphide is formed in the initial reaction, but definite proof is lacking.

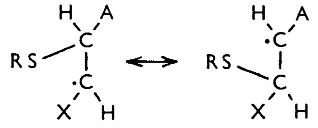
Oxidation of the sulphide (oily or crystalline) with hydrogen peroxide in hot acetic acid gave *trans*-1 : 2-dibenzoylethylene, no sulphone being obtained. Addition of toluene-ω-thiol to *trans*-1 : 2-dibenzoylethylene, initiated by ascaridole, gave benzyl 1 : 2-dibenzoylethyl sulphide, oxidised in the cold to the sulphone in good yield; but oxidation in hot acetic acid gave a reduced yield of sulphone together with *trans*-1 : 2-dibenzoylethylene.

(±)-1 : 2-Dibenzoylethyl α-methylphenethyl sulphide (m. p. 87·5°), benzyl 1 : 2-dibenzoylethyl sulphide, and the corresponding sulphones are stable in hot acetic acid; elimination of the sulphur-containing group is therefore an accompaniment of oxidation, and not a dissociation of the initial or final compound in the solvent.

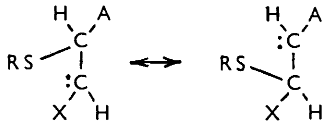
Addition of toluene-ω-thiol to 4′-nitrochalkone, initiated by ascaridole, gave benzyl 2-*p*-nitrobenzoyl-1-phenylethyl sulphide. From the product of the similar addition of (±)-1-phenylpropane-2-thiol there was isolated a single (±)-α-methylphenethyl 2-*p*-nitrobenzoyl-1-phenylethyl sulphide, $CH_2Ph{\cdot}CHMe{\cdot}S{\cdot}CHPh{\cdot}CH_2{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2$, though the low yield made it uncertain whether this diastereoisomer is the major product.

(±)-1-Phenylpropane-2-thiol did not react with coumarin (ascaridole, piperidine), benzylideneindene (ascaridole), or *iso*phorone (ascaridole).

The probable course of peroxide-initiated addition is set out in (I–VII). Q· denotes a radical formed by decomposition of ascaridole; (IV) and (V) represent diastereoisomeric intermediate radicals; these are resonance hybrids : *e.g.*, (IV) represents the resonance hybrid of forms (XI) and (XII); the results are however adequately described if (IV) is replaced by (XI) only, since the intermediate reacts through this form in the final stage, when, also, $C_{(\beta)}$ becomes symmetrical.



(XI) (XII)



(XIII) (XIV)

Dissymmetric addition has been discussed with respect to carbonyl reactions by Reid and Turner,[3] and to olefins in Part I.[4] In the present reaction the rates of formation of the diastereoisomeric intermediates (IV) and (V) will, in principle, differ, and the rates of reaction of (IV) and (V) with the asymmetric thiol, leading to (VI) and (VII), will also be different. However, the latter stage has no effect on the steric structure of (VI) and (VII), whence this rate difference is not significant from the standpoint of dissymmetry. The yields of (VI) and (VII) reflect, therefore, the rates at which (IV) and (V) are formed; and since these yields do not differ widely, neither do these rates.

The course of the piperidine-catalysed Michael reaction is closely analogous to that for the free-radical addition; the thiol-anion from the first stage :

$$[CH_2]_5{>}NH + CH_2Ph{\cdot}CHMe{\cdot}SH \longrightarrow [CH_2]_5{>}NH_2^+ + CH_2Ph{\cdot}CHMe{\cdot}S^-$$

affords intermediates similar to (IV) and (V), and in the final stage the conjugate acid of the base gives up a proton, yielding (VI) and (VII), and regenerates the base. The resonance hybrid of (XIII) and (XIV) replaces that of (XI) and (XII) in the above arguments.

Configurations assigned to the oily sulphides depend on retention of configuration during oxidation of the thiols, by hydrogen peroxide in acetic acid, to the crystalline sulphones. The isolation of the active sulphones precludes facile inversion at the asymmetric centres,

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[3] Reid and Turner, *J.*, 1949, 3365.
[4] Abbott and Arcus, *J.*, 1952, 1515.

since this would lead to racemic products. But to provide a more direct test, (—)-2 : 4-dinitrophenyl α-methylphenethyl sulphone, containing a single asymmetric centre, was heated in dry acetic acid at 100° : the rotatory power of the solution did not alter appreciably during 8 hr., and the sulphone was recovered substantially unchanged. In relation to this it may be noted that, whereas α-phenylsulphonylpropionic acid racemises in N-hydrochloric acid at 25°,[5] probably *via* the enolic form of the carboxyl group, α-phenylsulphonylethanesulphonic acid is optically stable in this solvent at 100°.[6]

EXPERIMENTAL

M. p.s are corrected. Heating for addition reactions was in a thermoregulated oil-bath at 100°, and for oxidations on a steam-bath. Hydrogen peroxide was the 34% aqueous solution. Specific rotations were determined with acetone solutions at *l* 0·5.

Additions.—β-*Nitrostyrene.* The β-nitrostyrene–thiol mixtures were heated under nitrogen which had been deoxygenated by passage through Fieser's solution.

(i) (±)-*Thiol.* β-Nitrostyrene (2·38 g.) and (±)-1-phenylpropane-2-thiol (2·38 g.) were heated with ascaridole (1 drop) for 5 hr., then chilled to −80°; a glass was formed which on treatment with light petroleum (b. p. 40—60°) crystallised. Recrystallisation of the product (1·8 g.; m. p. 66—70°) from the same solvent yielded (±)-α-*methylphenethyl* 2-*nitro*-1-*phenylethyl sulphide-A* (1·2 g.), m. p. 73—76°, which on further crystallisation formed rhombs, m. p. 76° (Found : C, 67·95; H, 6·35; N, 4·85; S, 10·3. $C_{17}H_{19}O_2NS$ requires C, 67·75; H, 6·35; N, 4·65; S, 10·7%). Evaporation of the first filtrate gave an oil from which crystals (0·6 g.; m. p. 40·5—42·5°) separated. After recrystallisation from ethanol they (0·34 g.) had m. p. 49·5—51·5°, and yielded on further crystallisation (±)-*sulphide-B*, rectangular plates, m. p. 53·5° (Found : C, 67·7; H, 6·35; N, 4·5; S, 10·55%). From filtrates two further crops were obtained : 0·16 g., m. p. 72—74·5°; 0·13 g., m. p. 49·5—52·5°. The total yield of sulphides was 44%.

In other experiments, β-nitrostyrene (2·65 g.) and (±)-1-phenylpropane-2-thiol (2·65 g.) gave (±)-sulphide-A (1·1 g.) and -B (0·52 g.), and 0·38 g. of each reactant gave (±)-sulphide-A (0·33 g.) and -B (0·24 g.) (A separating slowly and nearly completely before B crystallised).

β-Nitrostyrene (2·17 g.) and (±)-1-phenylpropane-2-thiol (2·17 g.) were heated with piperidine (3 drops) for 4¼ hr. Chilling did not induce crystallisation but treatment with methanol gave a solid and from the solvent two further crops separated; the combined material (1·2 g.; m. p. 65—69°) was crystallised from ethanol: (±)-sulphide-A (0·61 g.), m. p. and mixed m. p. 74·5—76°, was obtained. The filtrates yielded (±)-sulphide-B (0·30 g.), m. p. and mixed m. p. 52·5° (total yield of sulphides 34%).

Except for the first small-scale separation, above, the aggregate yield of identified sulphides is much below 100%, whence ratios of diastereoisomers cannot be calculated with sufficient certainty. Further, with regard to both sulphides and sulphones, compounds of series A are the less soluble, and hence more likely to be isolated completely.

The (±)-sulphide-A (0·50 g.) was heated in acetic acid (6 ml.) for 5 min. with hydrogen peroxide (3 ml.). The whole was then frozen to −80° and allowed to warm to room temperature: a product (0·33 g.), m. p. 114—115°, was obtained. After three recrystallisations from ethanol it yielded (±)-α-*methylphenethyl* 2-*nitro*-1-*phenylethyl sulphone-A*, needles, m. p. 117·5° (Found : O, 19·35; S, 9·6. $C_{17}H_{19}O_4NS$ requires O, 19·2; S, 9·6%). Similar oxidation of (±)-sulphide-B (0·35 g.) gave a product (0·15 g.), m. p. 100—100·5°, which after two recrystallisations from ethanol yielded (±)-*sulphone-B*, needles, m. p. 111° (Found : S, 9·55%). In each of these oxidations further sulphone was obtained on dilution of filtrates with water, and in neither was β-nitrostyrene encountered.

(ii) (+)-*Thiol.* β-Nitrostyrene (3·12 g.) and (+)-1-phenylpropane-2-thiol (α_{5893}^{17} +6·08°; *l*, 0·5) (3·14 g.) were heated with ascaridole (2 drops) for 6 hr. The product did not crystallise at −80°, on treatment with ethanol, methanol, and light petroleum, or on refrigeration for 7 months. This material (5·6 g.) was oxidised as described for the (−)-thiol. The solid product

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[5] Ramberg and Hedlund, *Arkiv Kemi, Min., Geol.*, 1938, **13**, *A*, No. 1, p. 11.

[6] Hedlund, *ibid.*, No. 12, p. 13.

(3·6 g.) was fractionally crystallised from ethanol; there were isolated (−)-*sulphone-A* (0·33 g.), needles, m. p. 140°, $[\alpha]_{5893}^{17}$ −46·5° (*c* 4·296) (Found: O, 19·25; S, 9·3%), and (+)-sulphone-B (not completely free from isomers; 0·12 g.), m. p. 79—83°, $[\alpha]_{5893}^{21}$ +74·6° (*c* 2·332).

(iii) (−)-*Thiol.* β-Nitrostyrene (5·33 g.) and (−)-1-phenylpropane-2-thiol (α_{5893}^{23} −13·46°; *l* 1·0) (5·33 g.) were heated with ascaridole (3 drops) for 6 hr. The product (which did not solidify) was heated in acetic acid (60 ml.) for 5 min. with hydrogen peroxide (40 ml.). The solution was chilled and poured into ice-cold water (1 l.). On fractional crystallisation from ethanol, it (7·6 g.) yielded (+)-*sulphone-A* (1·60 g.), needles, m. p. 139·5°, $[\alpha]_{5893}^{20}$ +47·0° (*c* 5·016) (Found: O, 19·0; S, 9·15%). The most soluble fraction, after draining on a porous plate, gave a solid (1·87 g.) of which three portions (total 1·19 g.) were subjected to vacuum-sublimation for 28 hr. β-Nitrostyrene (0·69 g.), m. p. 53·5—55·5° alone and when mixed with a specimen of m. p. 57°, sublimed; and there remained (−)-sulphone-B (0·33 g.), m. p. 100·5—102·5°, $[\alpha]_{5893}^{21}$ −89·1° (*c* 2·644).

β-Nitrostyrene and this thiol (each 4·39 g.) were heated with piperidine (4 drops) for 6¼ hr. The resultant oil was oxidised as above and the product (6·0 g.) fractionally crystallised from ethanol. It yielded (+)-sulphone-A (1·57 g.), m. p. 140°, $[\alpha]_{5893}^{22}$ +46·0° (*c* 5·046), and (−) *sulphone-B* (0·12 g.), m. p. 102·5°, $[\alpha]_{5893}^{20}$ −89·5° (*c* 2·478) (Found: O, 18·75; S, 9·15%). These specimens, when mixed with the corresponding specimens from the peroxidic addition, had m. p.s 139·5° and 101·5—102·5°.

A 1 : 1 mixture of (+)-sulphone-A and (−)-sulphone-A was optically inactive, and had m. p. 117—118° alone and when mixed with (±)-sulphone-A.

trans-1 : 2-*Dibenzoylethylene.* This compound (from National Aniline Division, Allied Chemical and Dye Corporation, New York) (7·6 g.), toluene-ω-thiol (4·0 g.), and ascaridole (2 drops) were heated under coal-gas for 5½ hr. The whole was allowed to crystallise from ethanol, and yielded *benzyl* 1 : 2-*dibenzoylethyl sulphide* (9·9 g.), needles, m. p. 97·5—98·5°, which after two further crystallisations had m. p. 99° (Found: C, 76·5; H, 5·55; S, 8·7. $C_{23}H_{20}O_2S$ requires C, 76·6; H, 5·6; S, 8·9%).

trans-1 : 2-Dibenzoylethylene (3·63 g.) and (±)-1-phenylpropane-2-thiol (2·43 g.) were heated with ascaridole (2 drops) under nitrogen for 6¼ hr. From a solution of the resultant oil in ethanol there separated a product (2·3 g.) having m. p. 80—81°, which after recrystallisation from light petroleum (b. p. 40—60°) and from ethanol yielded (±)-1 : 2-*dibenzoylethyl α-methylphenethyl sulphide* (1·27 g.), rhombs, m. p. 87·5° (Found: C, 76·8; H, 6·35; S, 7·95. $C_{25}H_{24}O_2S$ requires C, 77·3; H, 6·2; S, 8·25%). Evaporation of the filtrates gave a crop (0·37 g.), m. p. 84—85°, and an oil (3·2 g.). Similar reaction of the ethylene (3·33 g.) and the (±)-thiol (2·15 g.) gave solid sulphide (2·17 g.), m. p. 80—81°, and oil (2·8 g.).

(±)-1 : 2-Dibenzoylethyl α-methylphenethyl sulphide (oil; 0·40 g.), in acetic acid (5 ml.), was heated for 5 min. with hydrazine hydrate (100%; 4 drops). The solution was diluted (to 15 ml.) with water and air was aspirated through it for 10 min. The solid product, on crystallisation from chloroform–ethanol (1 : 5), gave a material (0·27 g.), m. p. 130—135°, containing sulphur, recrystallisation of which was accompanied by an odour of thiol and gave a product having m. p. 215—217°; it did not contain sulphur, and on further crystallisation yielded 3 : 6-diphenylpyridazine, m. p. 223—223·5° (Paal and Schulze [7] record m. p. 221—222°).

Oxidation of the sulphides. (±)-1 : 2-Dibenzoylethyl α-methylphenethyl sulphide (oil; 2·7 g.), in acetic acid (20 ml.), was heated for 10 min. with hydrogen peroxide (10 ml.). The solution, on being cooled to 0°, deposited yellow needles (0·4 g.), m. p. 103·5—105·5°, which after two crystallisations from ethanol had m. p. 109—110° and m. p. 111—112° when mixed with *trans*-1 : 2-dibenzoylethylene having m. p. 111·5°. On dilution of the filtrate with water (500 ml.) a further 0·9 g. of dibenzoylethylene was obtained.

The above sulphide (2·2 g.) was kept for 16 hr. at room temperature in acetic acid (20 ml.) containing hydrogen peroxide (4 ml.). An oil having separated, the whole was heated for 2 min., becoming homogeneous; the solution was poured into cold water (1 l.). The solid product was collected and recrystallised from methanol, yielding (±)-1 : 2-*dibenzoylethyl α-methylphenethyl sulphone* (1·2 g.), m. p. 116°, which on further crystallisation formed rhombs, m. p. 122·5—123° (Found: O, 15·15; S, 7·55. $C_{25}H_{24}O_4S$ requires O, 15·25; S, 7·6%).

The (±)-sulphide of m. p. 87·5° was oxidised as in the last two experiments. On being heated with hydrogen peroxide this sulphide (0·68 g.) gave *trans*-1 : 2-dibenzoylethylene (0·17 g.), m. p. and mixed m. p. 108—109·5°. In the cold, the sulphide (0·25 g.) yielded (±)-sulphone

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[7] Paal and Schulze, *Ber.*, 1900, **33**, 3795.

(0·12 g.), m. p. 115—116°, which after two recrystallisations from methanol had m. p. 119—120°, mixed m. p. 122°.

A solution of (±)-1 : 2-dibenzoylethyl α-methylphenethyl sulphide (m. p. 87·5°; 0·50 g.) in acetic acid (10 ml.) was heated for 1 hr. and then poured into ice-water (50 ml.). The sulphide (0·41 g.) was recovered, having m. p. and mixed m. p. 86—87°. From the similar treatment of a solution of the (±)-sulphone (0·25 g.), in acetic acid (12 ml.), there was recovered sulphone (0·22 g.), m. p. 117—119°; after recrystallisation from methanol it (0·19 g.) had m. p. and mixed m. p. 121—122°.

Benzyl 1 : 2-dibenzoylethyl sulphide (4·0 g.), in acetic acid (30 ml.), was heated for 10 min. with hydrogen peroxide (20 ml.). From the cooled solution there separated crystals (2·7 g.), fractional crystallisation of which from ethanol gave two crops (total 1·75 g.) of m. p. 173·5—175·5°, and two (total 0·80 g.) of m. p. 97·5—103·5°. Further crystallisation of the former yielded *benzyl* 1 : 2-*dibenzoylethyl sulphone*, needles, m. p. 175·5° (Found: C, 70·5; H, 5·3; S, 8·25. $C_{23}H_{20}O_4S$ requires C, 70·4; H, 5·15; S, 8·15%), and of the latter, *trans*-1 : 2-dibenzoylethylene, m. p. 108·5—111°, mixed m. p. 110—112°.

The preceding sulphide (1·0 g.), acetic acid (20 ml.), and hydrogen peroxide (3·5 ml.) were heated for 2 min. The homogeneous solution obtained was chilled in ice-water, then allowed to attain room temperature overnight. There separated benzyl 1 : 2-dibenzoylethyl sulphone (0·9 g.), m. p. 165°; after recrystallisation from ethanol it (0·77 g.) had m. p. 175·5°.

A solution of benzyl 1 : 2-dibenzoylethyl sulphide (1·0 g.) in acetic acid (10 ml.) was heated for 2 hr., then diluted with water (15 ml.); the sulphide (0·97 g.) was recovered, having m. p. 95·5° and mixed m. p. 98·5°. A solution of benzyl 1 : 2-dibenzoylethyl sulphone (0·34 g.) in acetic acid (10 ml.) was similarly treated; the sulphone (0·30 g.) was recovered, having m. p. 171·5°, mixed m. p. 172·5°.

4′-Nitrochalkone.—This compound (m. p. 149—150°; 2·1 g.) and toluene-ω-thiol (1·0 g.) were heated with ascaridole (2 drops) under coal-gas for 5¼ hr. The mixture was allowed to crystallise from light petroleum (b. p. 40—60°), and yielded a product (2·6 g.), m. p. 81—82°, which after three recrystallisations from ethanol gave *benzyl* 2-p-*nitrobenzoyl*-1-*phenylethyl sulphide*, needles, m. p. 87° (Found: N, 3·7; S, 8·5. $C_{22}H_{19}O_3NS$ requires N, 3·8; S, 8·05%).

4′-Nitrochalkone (8·4 g.) and (±)-1-phenylpropane-2-thiol (5·1 g.) were heated under nitrogen with ascaridole (4 drops) for 6 hr. From a solution of the product, an oil, in ethanol, there separated material (10·0 g.), m. p. 48—49°, which, after two crystallisations from methanol and four from *cyclo*hexane yielded (±)-*α-methylphenethyl* 2-p-*nitrobenzoyl*-1-*phenylethyl sulphide* (0·65 g.), needles, m. p. 81—82° (Found: C, 71·1; H, 5·9; S, 7·3. $C_{24}H_{23}O_3NS$ requires C, 71·15; H, 5·7; S, 7·9%).

(−)-2 : *4-Dinitrophenyl α-Methylphenethyl Sulphone.*—(−)-1-Phenylpropane-2-thiol (α^{17}_{5893} −5·88°; *l* 0·5) (1·95 g.), chloro-2 : 4-dinitrobenzene (2·6 g.) and sodium hydroxide (0·5 g.) were heated in ethanol (17·5 ml.) and water (2·5 ml.) for 10 min. The hot solution was filtered, and from the filtrate there separated (−)-2 : 4-*dinitrophenyl α-methylphenethyl sulphide* (3·2 g.), yellow rhombs, m. p. 84°, which after two recrystallisations from ethanol had m. p. 88°, $[\alpha]^{21}_{5893}$ −82·5° (*c* 4·848) (Found: N, 8·85; S, 9·85. $C_{15}H_{14}O_4N_2S$ requires N, 8·8; S, 10·05%).

The (±)-thiol (0·87 g.) similarly gave a (±)-*sulphide* (1·68 g.), m. p. 87—89°, which, after two recrystallisations from ethanol, formed yellow rhombs, m. p. 93—94° (Found: N, 8·9; S, 10·15%).

The above (−)-sulphide (1·2 g.), heated for 1½ hr. with hydrogen peroxide (5 ml.) in acetic acid (10 ml.), gave (−)-2 : 4-*dinitrophenyl α-methylphenethyl sulphone* (0·5 g.), needles, m. p. 169°, $[\alpha]^{19}_{5893}$ −32·2° (*c* 3·165). Crystallisation from ethanol did not change these constants (Found: O, 27·3; S, 8·85. $C_{15}H_{14}O_6N_2S$ requires O, 27·4; S, 9·15%).

A solution of the (−)-sulphone (0·457 g.) in acetic acid of m. p. 16·45° (7·4 ml. at 20°) was placed in a 1-dm. jacketed polarimeter tube with sealed end-plates, kept at 100° by steam. In 8¼ hr. α^{100}_{5893} −0·62° changed only to −0·60°. The solution was poured into cold water (200 ml.); there was recovered (−)-2 : 4-dinitrophenyl α-methylphenethyl sulphone (0·42 g.), $[\alpha]^{17}_{5893}$ −32·8° (*c* 5·010), m. p. and mixed m. p. 165°.

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