653. *Olefinic Acids. Part VII. The Addition of Thiols to Propiolic and Acetylenedicarboxylic Acid.*

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The addition of toluene-ω-thiol to propiolic acid has been studied under a variety of conditions; three main products are obtained, *viz.*, cis-, trans-, and (cis- + trans-)*β-benzylthioacrylic acid*, each of which on hydrogenation yields β-benzylthiopropionic acid, whilst oxidation gives *β-benzylsulphinyl-* and then *β-benzylsulphonyl-acrylic acid.* With thiolacetic acid, propiolic acid forms cis- and trans-*β-acetylthioacrylic acid*; the cis- and trans-*methyl* esters, accompanied by the diadduct, methyl αβ-bisacetylthiopropionate, are similarly obtained from methyl propiolate. With 2 mols. of thiolacetic acid, acetylenedicarboxylic acid gives a good yield of the diadduct, *αα'-bisacetylthiosuccinic acid,* hydrolysed to *αα'-dimercaptosuccinic acid* ("*dithiotartaric acid*"); from methyl acetylenedicarboxylate, both the *meso-* and the DL-form of *methyl αα'-bisacetylthiosuccinate* have been isolated. In the formation of the diadducts, the addition of the second molecule of thiol therefore takes place in an "abnormal" direction.

In Part II (Owen and Somade, *J.*, 1947, 1030) it was shown that α-bromoacrylic acid reacted with toluene-ω-thiol in pyridine to give β-benzylthioacrylic acid, and with thiolacetic acid to give α-bromo-β-acetylthiopropionic acid. Similar reactions were also carried out by Owen and Sultanbawa on α-bromo-γ-methoxycrotonic acid (Part VI, preceding paper). The formation of β-benzylthioacrylic acid clearly involves the addition of toluene-ω-thiol, followed by elimination of hydrogen bromide, though the structure was not proved. In order to prepare further quantities of this compound, and to investigate the possible existence of *cis-* and *trans-*isomers, the addition of toluene-ω-thiol to propiolic acid was explored as a possible alternative route.

There have been few investigations on the addition of thiols to acetylenic compounds. Ruhemann and Stapleton (*J.*, 1900, **77**, 1179) by the addition of sodium thiophenoxide to ethyl phenylpropiolate obtained a mono-adduct (I), and by a similar addition to ethyl acetylenedicarboxylate they prepared a mono- (II) and a di-adduct (III); the structure of (III) was not

$PhS\cdot CPh{:}CH\cdot CO_2Et$ (I.)

$CO_2Et\cdot C(SPh){:}CH\cdot CO_2Et$ (II.)

$CO_2Et\cdot C(SPh)_2\cdot CH_2\cdot CO_2Et$ (III.)

proved and the di-adduct may well have been the αα'-bisphenylthiosuccinic ester, particularly in view of the known tendency for an "abnormal" direction of addition of thiols to olefins. The remaining publications on this subject have concerned the addition of thiols to acetylenic hydrocarbons (Carothers, *J. Amer. Chem. Soc.*, 1933, **55**, 2008; Kohler and Potter, *ibid.*, 1935, **57**, 1316; Bader, Cross, Heilbron, and Jones, this vol., p. 619; B.I.O.S., F.D. 3781/45), acetylenic ketones (Ruhemann, *J.*, 1905, **87**, 467; Bowden, Braude and Jones, *J.*, 1946, 946), and acetylenic ethers (Bader *et al.*, *loc. cit.*).

The addition of toluene-ω-thiol to propiolic acid (IV) can theoretically yield three possible mono-adducts, the α- (V), and the *cis-* and *trans-*β-compounds (VI). Preliminary experiments, in the presence of various catalysts, appeared to indicate that three different crystalline mono-adducts were in fact formed, but subsequent investigation proved that these were *cis-* (VI), the *trans-* (VI), and the *cis-* + *trans-*compound (VI); no evidence has been obtained of the formation of the α-compound (V). With molar proportions of acid and thiol, a liquid by-product was usually formed, probably containing a di-adduct, but this was not examined. The yield of mono-adduct, based on thiol, was generally improved by the use of an excess of propiolic acid.

The use of peroxide catalysts favoured the formation of *cis-* (VI). Thus, on heating the reactants with 3% of benzoyl peroxide the resulting mixture yielded some pure cis-β-*benzylthio-*

acrylic acid, m. p. 144—145°. When, however, 5% of ascaridole was used as catalyst, this isomer formed the major part of the reaction product. In the presence of a small amount

$$\begin{tikzcd}
 & \underset{\text{(IV.)}}{HC\vdots C\cdot CO_2H} \arrow[r] & \underset{\text{(VI.)}}{CH_2Ph\cdot S\cdot CH{:}CH\cdot CO_2H} \arrow[r] \arrow[d] & \underset{\text{(VII.)}}{CH_2Ph\cdot S\cdot CH_2\cdot CH_2\cdot CO_2H} \\
 & \underset{\text{(V.)}}{CH_2{:}C(S\cdot CH_2Ph)\cdot CO_2H} & \underset{\text{(VIII.)}}{CH_2Ph\cdot SO\cdot CH{:}CH\cdot CO_2H} \arrow[r] & \underset{\text{(IX.)}}{CH_2Ph\cdot SO_2\cdot CH{:}CH\cdot CO_2H}
\end{tikzcd}$$

of sulphuric acid, a preponderance of the *trans*-β-benzylthioacrylic acid, m. p. 162—163°, was formed, identical with the compound of similar m. p. described in Part II (*loc. cit.*). With only a trace of sulphuric acid, the product consisted mainly of the *cis–trans*-mixture, m. p. *ca.* 126—127°, which could not be effectively separated by crystallisation and was at first mistaken for a third isomer. It was, however, smoothly converted into the *trans*-acid by heating it alone, or preferably in acetic acid with a trace of hydrogen chloride; a similar conversion was carried out on the pure *cis*-acid. The choice of the acid, m. p. 144—145°, rather than of that, m. p. 126—127°, as the individual stereoisomer follows from the observation that the m. p. of the former was depressed to that of the latter when mixed with an equal weight of the pure *trans*-acid; this is confirmed by the absorption spectra, the data for the acid of m. p. 126—127° being intermediate between those of the other two (see Table).

Conclusive proof that the three crystalline acids were all β-substituted compounds was afforded by hydrogenation in the presence of a large amount of palladium–charcoal (cf. Mozingo *et al.*, *J. Amer. Chem. Soc.*, 1945, **67**, 2092); each gave β-benzylthiopropionic acid (VII), identical with a synthetic sample prepared by the method of Schönberg and Iskander (*J.*, 1942, 90), and different from *α-benzylthiopropionic acid* synthesised from the potassium salt of toluene-ω-thiol and sodium α-bromopropionate.

Oxidation of β-benzylthioacrylic acid (VI) with hydrogen peroxide gave *β-benzylsulphinyl-* (VIII) and *β-benzylsulphonyl-acrylic acid* (IX).

The only published work on the addition of thiolacetic acid to acetylenic compounds is that of Bader *et al.* (*loc. cit.*), who obtained mono- and di-adducts; the latter were shown to be vicinal bisacetylthio-compounds, the addition of the second molecule of thiolacetic acid having proceeded "abnormally." The addition to acetylenic acids was not described. In view of the successful results, outlined above, on the addition of toluene-ω-thiol to propiolic acid, the reaction of this acid with thiolacetic acid has now been investigated. The *cis*- (m. p. 118·5—120°) and the *trans*- (m. p. 149—150°) form of *β-(acetylthio)acrylic acid* were obtained, together with a liquid product which probably contained the di-adduct. The reaction proceeded more smoothly with methyl propiolate to give *methyl* cis- (m. p. 58°) and trans- (m. p. 84·5°) *β-acetylthioacrylate* (X) and methyl αβ-bisacetylthiopropionate (XI).

$$CH\vdots C\cdot CO_2Me \longrightarrow \underset{\text{(X.)}}{AcS\cdot CH{:}CH\cdot CO_2Me} \longrightarrow \underset{\text{(XI.)}}{AcS\cdot CH_2\cdot CH(SAc)\cdot CO_2Me}$$

The ready formation of the vicinal di-adduct (XI), by "abnormal" addition, suggested the possibility of preparing an analogous compound from acetylenedicarboxylic acid or its ester. When this acid was treated with 2 mols. of thiolacetic acid, in ethyl acetate, a solid product gradually separated. This was *αα′-bisacetylthiosuccinic acid* (XII), which appeared to be a mixture of two forms (presumably *meso*- and DL-) but as separation was not readily achieved the

$$CO_2H\cdot C\vdots C\cdot CO_2H \longrightarrow \underset{\text{(XII.)}}{CO_2H\cdot CH(SAc)\cdot CH(SAc)\cdot CO_2H} \longrightarrow \underset{\text{(XIII.)}}{CO_2H\cdot CH(SH)\cdot CH(SH)\cdot CO_2H}$$

$$\underset{\text{(XIV.)}}{CO_2Me\cdot CH(SAc)\cdot CH(SAc)\cdot CO_2Me}$$

material was hydrolysed with aqueous hydrochloric acid to the dithiol, *αα′-dimercaptosuccinic acid* (XIII). The preparation of this substance was of interest, since in the course of the investigations on the synthesis of dithiols as anti-arsenicals (*inter al.*, Evans, Fraser, and Owen, this vol., p. 248), unsuccessful attempts had been made to obtain it by replacement reactions on αα′-dihalogenosuccinic acids and esters.

From the reaction of methyl acetylenedicarboxylate with thiolacetic acid, *methyl αα′-bisacetylthiosuccinate* (XIV) was obtained in *meso*- and DL-forms, though individual allocation of stereochemical structures was not possible.

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
cis-$CH_2Ph{\cdot}S{\cdot}CH{:}CH{\cdot}CO_2H$	2840	13,000
trans- ,, ,,	2750	21,000
cis- + *trans*- ,,	2810	16,000
$CH_2Ph{\cdot}SO{\cdot}CH{:}CH{\cdot}CO_2H$	2190	16,500
	2600	6,000
$CH_2Ph{\cdot}SO_2{\cdot}CH{:}CH{\cdot}CO_2H$	2650	6,000
$CO_2H{\cdot}CH(SAc){\cdot}CH(SAc){\cdot}CO_2H$	2300	9,000
$CO_2Me{\cdot}CH(SAc){\cdot}CH(SAc){\cdot}CO_2Me$, m. p. 119·5—120·5°	2290	9,000
$CO_2Me{\cdot}CH(SAc){\cdot}CH(SAc){\cdot}CO_2Me$, m. p. 71—72°	2280	10,000
cis-$AcS{\cdot}CH{:}CH{\cdot}CO_2H$	2680	10,500
trans- ,, ,,	2650	16,000
	2270	5,000
cis-$AcS{\cdot}CH{:}CH{\cdot}CO_2Me$	2690	18,500
	2770	17,000
trans- ,, ,,	2670	18,000
$AcS{\cdot}CH_2{\cdot}CH(SAc){\cdot}CO_2Me$	2300	8,000

Light-absorption data in alcohol, determined by Dr. E. A. Braude, are recorded in the Table; the allocations of the *cis*- and *trans*-structures to the stereoisomeric pairs, on the basis of relative melting points, are supported by these values, since the *cis*-compounds show maximum absorption at longer wave-lengths than their *trans*-isomers (cf. Part VI, *loc. cit.*).

EXPERIMENTAL.

(Light petroleum, unless otherwise stated, was the fraction of b. p. 40—60°.)

Propiolic Acid.—Hydrated ferric nitrate (2 g.) and sodium (3·5 g.) were added to liquid ammonia (1·5 l.), followed, after 5 minutes, by more sodium (42·5 g.). A rapid stream of acetylene was passed through the deep-blue solution until the colour became black. Ether (500 c.c.) was added, and the ammonia was allowed to evaporate off, more ether being added as required. The ethereal suspension of sodium acetylide was transferred to an autoclave, together with an excess of solid carbon dioxide, and stirred for 72 hours; the pressure, which initially rose to 25 atm., had then fallen to 20 atm. The product was then acidified with 5N-sulphuric acid, then saturated with sodium sulphate, and continuously extracted with ether, to yield 75 g. of propiolic acid, b. p. 80—88°/50 mm.

Addition of Toluene-ω-thiol to Propiolic Acid.—(*a*) A mixture of propiolic acid (0·7 g.), toluene-ω-thiol (0·63 g.), and benzoyl peroxide (0·02 g.) (acid : thiol = 2 : 1) was heated at 80° for 45 minutes, whereupon it partly solidified. After draining on porous tile, the solid (0·68 g., 50% based on thiol) was extracted with hot carbon tetrachloride; the insoluble portion crystallised from benzene in plates (0·1 g.) and was the *cis*-monoadduct, m. p. 139—145°, obtained in a purer form in a later experiment. The carbon tetrachloride extracts deposited needles (0·26 g.), m. p. 126—127°, of the *cis*- + *trans*-forms (see below). The yields of crude solid under identical conditions, with the same amounts of acid and catalyst, but with acid : thiol ratios of 1 : 1 and 1 : 2, were 55 and 35% respectively.

(*b*) A mixture of propiolic acid (4·2 g.), toluene-ω-thiol (7·4 g.), and ascaridole (0·2 g.) (acid : thiol = 1 : 1) was heated under reflux for 1½ hours on the steam-bath. The solid (5·45 g., 47%) obtained by draining the product on porous tile gave, on recrystallisation from carbon tetrachloride, long needles (3·5 g.) of cis-*β-benzylthioacrylic acid*, m. p. 144—145° (Found: C, 61·9; H, 5·2; S, 16·0. $C_{10}H_{10}O_2S$ requires C, 61·8; H, 5·2; S, 16·5%). Light absorption: see Table. The mother-liquors gave 0·6 g. of the *cis*- + *trans*-material, m. p. 125—126°.

(*c*) A mixture of propiolic acid (0·7 g.), toluene-ω-thiol (0·63 g.), and sulphuric acid (0·02 g.) (acid : thiol = 2 : 1) was set aside for 3 days. The pasty material so obtained was drained on porous tile, and the crude solid (0·96 g., 97%) was recrystallised from a large volume of hot carbon tetrachloride, to give needles, m. p. *ca.* 155—160°, raised to 158—164° (0·29 g.) on washing with hot carbon tetrachloride; recrystallisation from benzene then gave *trans*-*β*-benzylthioacrylic acid, m. p. 162—163°, undepressed on admixture with the specimen obtained by Owen and Somade (*loc. cit.*) (Found: S, 16·7. Calc. for $C_{10}H_{10}O_2S$: S, 16·5%). Light absorption: see Table. The carbon tetrachloride mother-liquors deposited 0·12 g. of material, m. p. 126—133°. With an acid : thiol ratio of 1 : 1, the yield of crude product was reduced to 48%.

(*d*) Propiolic acid (0·7 g.) was mixed with toluene-ω-thiol (0·62 g.) (acid : thiol = 2 : 1) and a trace (*ca.* 2 mg.) of sulphuric acid was added. After a few days, the solid (0·77 g., 80%) was separated and crystallised from carbon tetrachloride in needles of the *cis*- + *trans*-form, m. p. 125—127°, unaltered on repeated crystallisation (Found: C, 61·3; H, 5·3; S, 16·5. $C_{10}H_{10}O_2S$ requires C, 61·8; H, 5·2; S, 16·5%). Light absorption, see Table. With 1 : 1 and 1 : 2 ratios of acid : thiol the products after recrystallisation also had m. p. 125—127°, though the yields were only 29 and 19% respectively. With an 8 : 1 ratio, however, the product (yield, 79%) gave needles, m. p. 140—153°, which evidently contained a higher proportion of the *trans*-form.

(*e*) A mixture of propiolic acid (0·8 g.), toluene-ω-thiol (0·66 g.) (acid : thiol = 2 : 1), and 4N-sulphuric acid (0·01 c.c.) was set aside for 3 days at room temperature. The solid (0·74 g., 72%) was collected and crystallised from carbon tetrachloride in needles of the *cis*- + *trans*-form, m. p. 126—127°. A small less-soluble fraction was recrystallised from benzene and formed plates of the *cis*-form, m. p. 144°. With an acid : thiol ratio of 1 : 1 the crude yield was 18%.

Conversion of cis- *into* trans-*Acid.*—(*a*) The *cis*- + *trans*-mixture, m. p. 126—127° (0·1 g.), was heated at 150° for ½ hour; two recrystallisations from benzene gave the *trans*-acid, m. p. and mixed m. p. 162°.

(*b*) The *cis*- + *trans*-acid (1 g.), in acetic acid (5 c.c.) containing a trace of hydrogen chloride, was heated on the steam-bath for 6 hours. The product was precipitated by the addition of water and on crystallisation from benzene gave the *trans*-acid, m. p. 155—157°, raised on further recrystallisation to 162—163°.

(*c*) The pure *cis*-acid (0·15 g.), on similar treatment with hydrogen chloride in acetic acid for 4 hours at 100°, gave the *trans*-acid, m. p. 164—165°.

α-Benzylthiopropionic Acid.—A solution of α-bromopropionic acid (1·5 g.) in alcohol (10 c.c.) was added to a solution of toluene-ω-thiol (2·5 g.) and potassium hydroxide (1·1 g.) in alcohol (20 c.c.). Separation of sodium bromide began immediately, and after the mixture had been heated on the steam-bath for 15 minutes the solvent was evaporated, and the residue dissolved in sodium hydrogen carbonate solution and extracted with ether, these extracts being rejected. The aqueous solution was then acidified and extracted with ether to yield a solid residue of *α-benzylthiopropionic acid*, which formed large prisms, m. p. 78—79°, from light petroleum (b. p. 60—80°) (Found: C, 61·3; H, 5·9. $C_{10}H_{12}O_2S$ requires C, 61·2; H, 6·15%).

Hydrogenation of the β-Benzylthioacrylic Acids.—(*a*) The *cis*- + *trans*-acid (0·1 g.) in methanol (50 c.c.) was hydrogenated at ordinary temperature and pressure, in the presence of 10% palladium–charcoal (2·6 g.) (cf. Mozingo *et al.*, *loc. cit.*). Absorption ceased after 40 minutes, and the filtered solution was evaporated to a solid; extraction with light petroleum left a small residue, m. p. 140—157°, possibly unchanged starting material (if this is so, the *cis*-form would appear to be preferentially hydrogenated). Concentration of the light petroleum extracts gave leaflets (0·03 g.) of β-benzylthiopropionic acid, m. p. 81—83°, undepressed on admixture with an authentic sample prepared by the method of Schönberg and Iskander (*J.*, 1942, 90) but showing a large depression on admixture with the α-isomer. The low recovery must be attributed to extensive loss by adsorption on the large amount of catalyst necessary for the reduction.

(*b*) The pure *cis*-acid (0·15 g.) was similarly treated in methanol (75 c.c.) in the presence of the catalyst (4 g.). Extraction of the product with light petroleum gave 0·045 g. of β-benzylthiopropionic acid, m. p. and mixed m. p. 81—82°.

(*c*) The *trans*-acid (0·15 g.) similarly gave 0·015 g., m. p. and mixed m. p. 81—82°. The exceptionally low yield again suggests that the *trans*-acid is hydrogenated less readily.

Oxidation of β-Benzylthioacrylic Acid.—(*a*) The *cis*- + *trans*-acid (0·2 g.) was dissolved in acetic acid (3 c.c.) and mixed with 30% hydrogen peroxide (0·8 c.c.). A white precipitate rapidly formed. After 12 hours it was collected and crystallised from methanol, to give large prisms of *β-benzylsulphinylacrylic acid*, m. p. 164° (Found: S, 15·2. $C_{10}H_{10}O_3S$ requires S, 15·25%). Light absorption: see Table. The mother-liquor, on dilution with water and extraction with ether, gave flakes of the sulphone (described below), m. p. 192—194°.

(*b*) The acid (0·5 g.) in acetic acid (7 c.c.) was treated with 30% hydrogen peroxide (1·2 c.c.). The precipitate gradually redissolved, and after 3 days had disappeared. Water (15 c.c.) was added, and on cooling in ice the *β-benzylsulphonylacrylic acid* (0·17 g.) separated, m. p. 193—194° after recrystallisation from aqueous methanol (Found: C, 53·5; H, 4·5; S, 14·1. $C_{10}H_{10}O_4S$ requires C, 53·1; H, 4·45; S, 14·2%). Light absorption: see Table. The same sulphoxide and sulphone were obtained from both the *cis*- and the *trans*-form of β-benzylthioacrylic acid.

Addition of Thiolacetic Acid to Propiolic Acid.—A mixture of propiolic acid (0·7 g.) and thiolacetic acid (1·9 g.) was set aside for 2 weeks, and the excess of thiolacetic acid was then removed under reduced pressure. The residue (2·1 g.) contained a small amount of solid, which was collected and crystallised from light petroleum (b. p. 80—100°) in small prisms of trans-*β-acetylthioacrylic acid* (0·03 g.), m. p. 149—150° (Found: C, 41·0; H, 4·2; S, 21·6. $C_5H_6O_3S$ requires C, 41·1; H, 4·15; S, 21·9%). Light absorption: see Table. The liquid portion was distilled at 120° (bath temp.)/0·0001 mm., and deposited some solid; recrystallisation from light petroleum (b. p. 80—100°) gave cis-*β-acetylthioacrylic acid*, m. p. 118·5—120° (Found: C, 41·0; H, 4·5; S, 21·5. $C_5H_6O_3S$ requires C, 41·1; H, 4·15; S, 21·9%). Light absorption: see Table.

Addition of Thiolacetic Acid to Methyl Propiolate.—A mixture of methyl propiolate (6·4 g.) and thiolacetic acid (13·8 g.) was set aside for a week and then heated on the steam-bath for 1 hour. Removal of excess thiolacetic acid under reduced pressure, and fractionation of the residue gave (i) 1·0 g., b. p. 62—65°/0·4 mm., and (ii) 9·5 g. at 120° (air bath temp.)/0·4 mm. The first fraction solidified completely and on recrystallisation from ethanol gave large prisms of *methyl* cis-*β-acetylthioacrylate*, m. p. 58—58·5° (Found: C, 44·9; H, 4·9. $C_6H_8O_3S$ requires C, 45·0; H, 5·0%). Light absorption: see Table. The second fraction, a deep-red liquid, deposited 2·2 g. of a colourless solid, which on recrystallisation from alcohol furnished the trans-*isomer*, m. p. 84·5° (Found: C, 45·1; H, 4·65; S, 19·4. $C_6H_8O_3S$ requires C, 45·0; H, 5·0; S, 20·0%). Light absorption: see Table. Refractionation of the liquid portion of (ii) gave a further quantity of this mono-adduct, b. p. 73°/0·5 mm., followed by methyl αβ-bisacetylthiopropionate (3·1 g.), b. p. 83—84°/0·001 mm., n_D^{22} 1·5201 (light absorption: see Table); the latter was converted into methyl αβ-dimercaptopropionate, b. p. 52°/0·5 mm., n_D^{24} 1·5192, by treatment with 1% methanolic hydrogen chloride at room temperature for 3 days [Found: S(H), 40·25. Calc. for $C_4H_8O_2S_2$: S(H), 42·15%] (Pavlic, U.S.P. 2,408,094, gives b. p. 54°/0·5 mm., n_D^{25} 1·5251).

Addition of Thiolacetic Acid to Acetylenedicarboxylic Acid.—A solution of acetylenedicarboxylic acid (5·8 g.) and thiolacetic acid (7·6 g.) in ethyl acetate (15 c.c.) was set aside for 8 days. The colourless solid (8·95 g.), which had then appeared, was collected and recrystallised from acetone to give small prisms of *αα′-bisacetylthiosuccinic acid*, m. p. 171—173° (Found: C, 36·2; H, 3·9; S, 23·45. $C_8H_{10}O_6S_2$ requires C, 36·1; H, 3·8; S, 24·1%). Light absorption: see Table. This material (3 g.) was heated under reflux for 1 hour with 1% aqueous hydrochloric acid (25 c.c.) under nitrogen. On cooling, a pale yellow solid (1 g.) was obtained, and a further small quantity was isolated by ether extraction. Recrystallisation from aqueous methanol gave colourless prisms of *αα′-dimercaptosuccinic acid*, m. p. 190—192° (decomp.) [Found: C, 26·1; H, 3·7; S, 34·2; S(H), 25·1. $C_4H_6O_4S_2$ requires C, 26·35; H, 3·3; S, 35·15%].

Addition of Thiolacetic Acid to Methyl Acetylenedicarboxylate.—A mixture of methyl acetylenedicarboxylate (1·46 g.) (cf. Jeffery and Vogel, *J.*, 1948, 678) and thiolacetic acid (1·69 g.) was set aside for 3 days. The large colourless crystals of *methyl αα′-bisacetylthiosuccinate* (0·45 g.) were collected and recrystallised from light petroleum (b. p. 80—100°) in prisms, m. p. 119·5—120·5° (Found: C, 40·9; H, 4·9; S, 21·7. $C_{10}H_{14}O_6S_2$ requires C, 40·8; H, 4·8; S, 21·8%). Light absorption: see Table. The liquid portion of the reaction mixture was then heated on the steam-bath for 2½ hours; after removal of low-boiling material, under reduced pressure, the residue partly solidified. The solid (1·3 g.) was drained on porous tile and dissolved in hot alcohol; on cooling, a small crop of colourless prisms, m. p. 90—110°, was obtained. Light petroleum (b. p. 60—80°) was then added, whereupon large rhombs were gradually deposited; recrystallisation from alcohol–light petroleum (b. p. 60—80°) gave the stereoisomeric *methyl aa′-bisacetylthiosuccinate*, m. p. 71—72° (Found: C, 41·0; H, 5·0; S, 20·2. $C_{10}H_{14}O_6S_2$ requires C, 40·8; H, 4·8; S, 21·8%). Light absorption: see Table.

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[*Received, July 6th,* 1949.]