NOTES.

Some Reactions of 3 : 5-*Di-iodoanisaldehyde.* By J. H. WILKINSON.

PRESSURE of other work having led to the abandonment of the project of synthesising sulphonic acid analogues of 3 : 5-di-iodotyrosine, it is considered desirable to report the results obtained. 3 : 5-*Di-iodoanisaldehyde* was prepared from 3 : 5-di-iodo-4-hydroxybenzaldehyde (Paal and Mohr, *Ber.*, 1895, **28**, 2407), and was reduced by the Meerwein–Pondorff method to 3 : 5-*di-iodo*-p-*methoxyphenyl alcohol.* With nitromethane the aldehyde gave 3 : 5-*di-iodo-β-nitro*-4-*methoxystyrene,* but it failed to react with sodium hydrogen sulphite.

The bisulphite compounds of anisaldehyde and phenylacetaldehyde reacted with ammonia (cf. McIlwain, *J.*, 1941, 75) to give the sulphonic acid analogues of *p*-methoxyphenylglycine and phenylalanine respectively.

Experimental.—(Microanalyses are by Drs. Weiler and Strauss, Oxford. M. p.s are uncorrected.)

3 : 5-*Di-iodoanisaldehyde dimethyl acetal.* 3 : 5-Di-iodo-4-hydroxybenzaldehyde (20 g.) was partly dissolved and partly suspended in a mixture of methanol (100 c.c.) and methyl sulphate (16 c.c.), cooled in an ice-bath. A solution of sodium hydroxide (8 g.) in water (15 c.c.) was added in one instalment and the mixture stirred. The temperature rose to about 70°. The solution was cooled and diluted with water whereupon the *acetal* (11·45 g.) separated. It crystallised from light petroleum (b. p. 40—60°) in pale yellow rhombs, m. p. 66° (Found : C, 27·9; H, 2·4; I, 59·8. $C_{10}H_{12}O_3I_2$ requires C, 27·7; H, 2·75; I, 58·6%). Acidification of the alkaline liquors precipitated unreacted 3 : 5-di-iodo-4-hydroxybenzaldehyde (7·3 g.).

3 : 5-*Di-iodoanisaldehyde.* The dimethyl acetal (5·9 g.) was heated under reflux with 2N-hydrochloric acid (25 c.c.) for 5 minutes. The solid was collected (5·29 g.) and crystallised from benzene, the *aldehyde* being obtained in buff-coloured needles, m. p. 124°, sparingly soluble in light petroleum (Found : C, 24·4; H, 1·8; I, 65·5. $C_8H_6O_2I_2$ requires C, 24·7; H, 1·6; I, 65·4%). When heated above its m. p., it underwent rapid oxidation to 3 : 5-di-iodo-*p*-anisic acid, m. p. 253° (Wheeler and

Liddle, *Amer. Chem. J.*, 1909, **42**, 441, report m. p. 255—256°). The 2 : 4-*dinitrophenylhydrazone* crystallised from aqueous dioxan in orange-red prisms, m. p. 270° (decomp.) (Found: N, 9·5. $C_{14}H_{10}O_5N_4I_2$ requires N, 9·85%). It was sparingly soluble in most organic solvents.

Attempted preparation of α-*amino*-α-(3 : 5-*di-iodo*-4-*methoxyphenyl*)*methanesulphonic acid.* 3 : 5-Di-iodoanisaldehyde (1 g.) was suspended in alcohol (5 c.c.) at 70° and treated with a solution of sodium hydrogen sulphite (0·3 g.; 20% excess). The mixture was shaken mechanically for 2 hours, and the temperature kept at 70°. Water (10 c.c.) was added to the cooled mixture and the unreacted aldehyde (0·95 g.) was recovered by filtration.

3 : 5-*Di-iodoanisyl alcohol.* 3 : 5-Di-iodoanisaldehyde (3·88 g.) was added to a solution of aluminium *iso*propoxide (0·4 g.) in anhydrous *iso*propyl alcohol (80 c.c.), the mixture heated under reflux for 2 hours and the acetone, produced in the reaction, then removed by distillation. After 7 hours no more acetone could be detected in the distillate by the 2 : 4-dinitrophenylhydrazine test. The solvent was removed and the cooled residue treated with 2N-hydrochloric acid (25 c.c.). The solid was collected, washed with 2N-hydrochloric acid and water, and dried ($CaCl_2$). Yield : 3·81 g. (98%). 3 : 5-Di-iodoanisyl alcohol crystallised from light petroleum (b. p. 60—80°) in colourless needles, m. p. 82°, highly soluble in alcohol and benzene (Found : C, 24·8; H 2·2; I 65·2. $C_8H_8O_2I_2$ requires C, 24·6; H, 2·05; I, 65·2%).

3 : 5-*Di-iodo*-4-*methoxybenzyl chloride.* The alcohol (1·7 g.) was dissolved in anhydrous benzene (5 c.c.) and heated under reflux with thionyl chloride (1·5 c.c.) for 1 hour. The excess of reagent and solvent were removed and the residue was dried at 50°/15 mm. Yield : 1·66 g. (93%). The *product* crystallised from light petroleum (b. p. 40—60°) in colourless needles, m. p. 74—75°, highly soluble in most organic solvents (Found : C, 23·9; H, 1·8. $C_8H_7OClI_2$ requires C, 23·5; H, 1·7%). An attempt to condense this with ethyl malonate in the presence of 1 equivalent of sodium ethoxide failed.

3 : 5-*Di-iodo*-β-*nitro*-4-*methoxystyrene.* 3 : 5-Di-iodoanisaldehyde (4 g.) was dissolved in alcohol (30 c.c.) and treated with nitromethane (0·62 g.). The mixture was cooled to 0° and sodium hydroxide (2·6 c.c., 5N. in 50% alcohol) was added dropwise with mechanical stirring, the temperature being kept below 10°. After 15 minutes, the mixture was diluted with ice-water and filtered from unchanged di-iodoanisaldehyde. The filtrate was added to 2N-hydrochloric acid (25 c.c.) and the solid collected. Yield : 1·8 g. (41%). It crystallised from 20% alcohol in pale yellow needles, m. p. 149° (Found : C, 25·1; H, 1·75; N, 3·3; I, 58·5. $C_9H_7O_3NI_2$ requires C, 25·1; H, 1·6; N, 3·25; I, 58·9%). This *nitrostyrene* (0·74 g.) in dioxan solution (6 c.c.) was added to 1·5M-sodium hydrogen sulphite (2 c.c.) and the solution shaken mechanically for 48 hours. Water (10 c.c.) was added to precipitate the unreacted nitrostyrene (0·41 g.) and the mixture centrifuged. The supernatant liquid was evaporated; the residue was dissolved in alcohol and filtered from a little sodium hydrogen sulphite. The alcohol was removed from the filtrate, but the highly water-soluble residue, believed to consist of sodium 2-nitro-1-(3 : 5-di-iodo-4-methoxyphenyl)ethane-1-sulphonate, could not be induced to crystallise.

α-*Amino*-α-p-*methoxyphenylmethanesulphonic acid.* The bisulphite compound [from distilled anisaldehyde (5·44 g.) and sodium hydrogen sulphite (4·16 g.)] was treated at 20° with ammonia (20 c.c., *d* 0·88) in a sealed tube for 1½ hours, followed by ½ hour at 50°. The mixture was cooled, filtered, and acidified at 0° with 10N-sulphuric acid. The solid which separated was collected, washed with 50% alcohol, alcohol, and ether, and dried at 20°/15 mm. Yield : 2·1 g. (24%). The addition of alcohol to the filtrate precipitated a further 3·8 g. (44%) but this was contaminated with ammonium sulphate. The main *product* was crystallised from water at a temperature not exceeding 70°—it separated in highly soluble colourless needles, m. p. 123° (decomp.) (Found : N, 6·55; S, 15·0. $C_8H_{11}O_4NS$ requires N, 6·45; S, 14·75%).

α-*Amino*-β-*phenylethanesulphonic acid* was prepared in a similar manner from redistilled phenylacetaldehyde. The product was sparingly soluble in water and on heating to promote solution, the compound decomposed to give a highly soluble substance, which appeared to be the ammonium salt of the α-hydroxy-acid. Purification of the required compound was therefore effected by successive trituration with water, alcohol, and ether. The product was a colourless powder, m. p. 147° (decomp.) (Found : N, 6·9; S, 15·3. $C_8H_{11}O_3NS$ requires N, 6·96; S, 15·9%).

The author wishes to acknowledge with thanks gifts of chemicals from Glaxo Laboratories Ltd. and Imperial Chemical Industries Ltd.—DEPARTMENT OF CHEMICAL PATHOLOGY, WESTMINSTER MEDICAL SCHOOL (UNIVERSITY OF LONDON), HORSEFERRY ROAD, LONDON, S.W.1. [*Received, May 5th*, 1949.]

The Diacrylate and Dimethacrylate of But-2-*yne*-1 : 4-*diol.*

By L. F. WIGGINS and D. J. C. WOOD.

SEVERAL esters and other derivatives of but-2-yne-1 : 4-diol have been described by Johnson (*J.*, 1946, 1009) and other aspects of the chemistry of this most interesting compound are recorded by Reppe (see " New Technical Applications of Acetylene ", H.M. Stationery Office, 1946). *But*-2-*yne*-1 : 4-*diol diacrylate* and the corresponding *dimethacrylate* were prepared from the alcohol and the requisite acid chloride in the presence of sodium hydroxide, and the product was extracted with ether. The diacrylate was a liquid and the dimethacrylate a crystalline solid of low melting point, both compounds being purified by distillation under reduced pressure. Both esters polymerised very readily, so much so that their isolation in good yield was difficult. Attempts to polymerise the dimethacrylate with poly(methyl methacrylate) according to the current practice in dental prosthetics were unsuccessful. Poly(methyl methacrylate) did not apparently dissolve in the monomeric butynediol dimethacrylate.

But-2-*yne*-1 : 4-*diol Diacrylate.*—Butynediol, m. p. 54°, (1 g.) was dissolved in sodium hydroxide solution (5N.; 8 c.c.), and acrylyl chloride (2 c.c.) added in small portions with shaking and cooling in an ice-bath. The ester separated as an oil, which was extracted with ether, the extract was dried ($MgSO_4$), and the solvent evaporated under reduced pressure, copper powder (0·5 g.) being added as a polymerisation inhibitor. *But*-2-*yne*-1 : 4-*diol diacrylate* (1·4 g.) distilled at 106—111° (bath temp.)/0·1 mm. as a colourless oil (0·4 g., 18%), n_D^{17} 1·4871 (Found : C, 62·0; H, 5·3. $C_{10}H_{10}O_4$ requires C, 61·9; H, 5·2%). The remainder of the crude product polymerised to a colourless gel before distillation was completed.

*But-2-yne-*1 : 4-*diol Dimethacrylate.*—Butynediol (2 g.) was dissolved in sodium hydroxide solution (5N.; 20 c.c.) and methacrylyl chloride (5·5 c.c.) added in small portions with shaking and cooling in an ice-bath. The oil which separated was extracted with ether, the extract was washed with water and dried ($MgSO_4$), and the ether was removed under reduced pressure in a stream of nitrogen and in the presence of copper powder (0·5 g.). The *but-2-yne-*1 : 4-*diol dimethacrylate* was distilled in nitrogen at 116—120° (bath temp.)/0·05 mm. and was obtained as a colourless oil (2·8 g.; 54%), n_D^{18} 1·4846, soluble in alcohol, benzene, chloroform, light petroleum, and ethyl acetate (Found: C, 64·8; H, 6·5. $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·3%). On refrigeration the ester crystallised completely. It was recrystallised with difficulty from aqueous alcohol and then had m. p. 28·5—29°. The ester polymerised very readily; it could be kept in the monomeric state for 1—2 weeks only, even at 0° in the presence of copper powder. Heating at 90—100° caused rapid decomposition accompanied by considerable increase in viscosity, copious evolution of fumes, and much charring. At 70—80°, however, with the addition of a little benzoyl peroxide, the ester remained fluid and apparently unchanged for a few minutes, and then was suddenly transformed into a colourless gel. Further heating gradually produced a clear, hard, very brittle resin, which was insoluble in organic solvents (*e.g.*, chloroform), and was not appreciably attacked by boiling concentrated nitric acid or aqua regia, but it slowly disintegrated in hot concentrated sodium hydroxide.

When the ester was heated in an atmosphere of nitrogen, polymerisation was appreciably retarded. Without this precaution it was extremely difficult to distil it, but even in the presence of nitrogen a second distillation resulted in only about half being recovered as the monomer.

The monomer showed no solvent action on granular poly(methyl methacrylate) during 20 minutes at room temperature. When warmed in a water-bath at 50° for about 10 minutes the mixture attained a doughlike consistency and polymerisation of this product at 100° gave a hard resin, but in this material the original poly(methyl methacrylate) granules were easily visible and the surrounding medium clearly consisted only of butynediol dimethacrylate which had polymerised without dissolving the granules.—THE A.E. HILLS LABORATORIES, THE UNIVERSITY, EDGBASTON, BIRMINGHAM, 15.

[*Received, May* 10*th*, 1949.]

The Interaction of the Silver Salts of Optically Active Acids with Bromine. By F. BELL and I. F. B. SMYTH.

IN view of the publication of a paper by Arnold and Morgan (*J. Amer. Chem. Soc.*, 1948, **70**, 4248) and of a letter by Arcus, Campbell, and Kenyon (*Nature*, 1949, **163**, 287) on this topic, results previously obtained by us are briefly communicated.

Silver (+)- and (—)-α-ethylhexoates in carbon tetrachloride suspension were converted by the action of bromine into 3-bromoheptane, which in all experiments proved to be optically inactive. This result agrees with that of Arnold and Morgan but is more conclusive in that the (+)- and (—)-ethylhexoic acids used were almost optically pure and, in the final experiments, the time of heating was considerably less.

Next, silver (+)- and (—)-diphenylsuccinates in carbon tetrachloride suspension were converted by the action of bromine into 1 : 2-dibromo-1 : 2-diphenylethane. The material isolated was mainly the relatively insoluble *meso*dibromo-derivative, m. p. 237°; the remainder (about 15%) was slightly impure inactive dibromodiphenylethane, m. p. 101—105° (Wislicenus and Seeler, *Ber.*, 1895, **28**, 2693, give m. p. 237° and 110° for the two isomers).

Silver (+)- and (—)-benzylethylacetates (α-benzylbutyrates) were similarly converted into 2-bromo-1-phenylbutane. The product from the (—)-salt was completely inactive but that from the (+)-salt showed the very small specific rotation of —2·8°. The salts were decomposed under apparently identical conditions and the reason for this difference is obscure.

Although the results of the present investigations might have been held to favour a free-radical mechanism for the replacement, this conclusion is entirely negatived by the work of Arcus, Campbell, and Kenyon, to whose views we subscribe.

Experimental.—*Silver* (+)- *and* (—)-*α-Ethylhexoates.*—Ethylhexoic acid was prepared and resolved by the method of Kenyon and Platt (*J.*, 1939, 633). Silver salts were prepared from acids of $[\alpha]_{5461}$ +9·79° and —9·9°. Many decomposition experiments were made and the following description represents the mildest conditions employed. Silver (+)-α-ethylhexoate (15 g.), dried *in vacuo* over phosphoric oxide and finely ground, was suspended in carbon tetrachloride (150 ml.) and treated with a solution of bromine (8 g.) in carbon tetrachloride (30 ml.) with external cooling. The mixture was heated under reflux for 15 minutes on the water-bath, filtered, and shaken with sodium hydroxide and water. Distillation yielded 3-bromo-*n*-heptane (4 g.), b. p. 51—54°/17 mm., n_D^{20} 1·4511 (Dillon and Lucas, *J. Amer. Chem. Soc.*, 1928, **50**, 1713, give b. p. 84—85°/74 mm., n_D^{20} 1·4507). The product was devoid of optical activity.

Silver (+)- *and* (—)-*Diphenylsuccinates.*—Diphenylsuccinic acid was resolved by crystallisation of the quinidine salt from 50% aqueous alcohol. Ten crystallisations yielded (+)-diphenylsuccinic acid, which on a further crystallisation from aqueous acetic acid had $[\alpha]_{5461}^{20}$ +351° (*c*, 1·0 in alcohol, $l = 1$).

Kolin (Ph.D. Thesis, Queen's University, Belfast, 1945) has briefly described the interaction of optically inactive silver diphenylsuccinate with bromine. His procedure and the following were applied to the optically active salts with essentially similar results.

Silver (+)-diphenylsuccinate (10·8 g.) was heated under reflux with bromine in carbon tetrachloride for 45 minutes. After filtration and washing with sodium hydroxide and water, the carbon tetrachloride was distilled, leaving a yellow pasty residue. Extraction with alcohol and recrystallisation of the soluble portion yielded a very small quantity of 1 : 2-dibromo-1 : 2-diphenylethane, m. p. 101—105°, which was optically inactive. Recrystallisation of the alcohol-insoluble portion from xylene gave the high-melting isomer, m. p. 237°, which is the principal product of the reaction.

Silver (+)- *and* (−)-*Benzylethylacetates.*—Benzylethylacetic acid was prepared by the reduction of phenylangelic acid (Baeyer and Jackson, *Ber.*, 1880, **13**, 118) and resolved by use of (−)-menthylamine (Pickard and Yates, *J.*, 1909, **95**, 1018). Silver (+)-benzylethylacetate (19 g.), obtained from the acid of $[\alpha]_{5461}$ +30·9°, was treated with bromine in carbon tetrachloride and heated under reflux for $\frac{1}{2}$ hour. After working up as before, 3 g. of 2-bromo-1-phenylbutane were obtained as a pale pink liquid, b. p. 110—115°/16 mm., n_D^{18} 1·5447 (Carter, *J. Biol. Chem.*, 1935, **108**, 619, records b. p. 98—99°/1 mm., n_D^{20} 1·5393). It had $[\alpha]_{5461}$ −2·85° (*c*, 14·37 in alcohol; *l* = 1). Treatment of silver (−)-benzylethylacetate in a precisely similar manner gave optically inactive 2-bromo-1-phenylbutane.

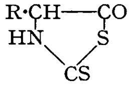
A decision to apply this method to optically active diphenic acids was abandoned when it was found that silver diphenate would not react smoothly with bromine to give 2 : 2′-dibromodiphenyl.

One of the authors (I. F. B. S.) is in receipt of a grant from the Department of Scientific and Industrial Research, for which he wishes to express his indebtedness.—College of Technolgogy, Belfast. [*Received, May* 10*th*, 1949.]

The Action of Thionyl Chloride on Some Esters of N-*Dithiocarboxyamino-acids.*

By Charles E. Dalgliesh.

The revival of interest in the Leuchs polymerisation of anhydrocarboxyamino-acids (Leuchs *et al.*, *Ber.*, 1906, **39**, 857; 1907, **40**, 3235; 1908, **41**, 1721; Woodward and Schramm, *J. Amer. Chem. Soc.*, 1947, **69**, 1551) suggested the investigation of dithio-compounds of type (I) which might also be expected to give polypeptides. By analogy such a compound should be formed on treatment of a *N*-dithiocarbalkoxyamino-acid $CS_2R''\cdot NH\cdot CHR'\cdot CO_2H$ (II), with thionyl chloride, followed by cyclisation.



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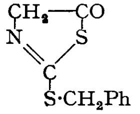

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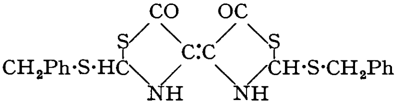

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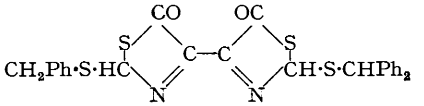

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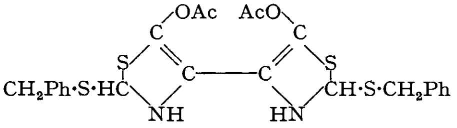


(VI.)

On treatment of *N*-dithiocarbobenzyloxyglycine (II; R′ = H, R″ = CH_2Ph) (Cook, Harris, Heilbron, and Shaw, *J.*, 1948, 1056) with thionyl chloride, the mixture became deep red, and readily gave brilliant scarlet needles in good yield. These contained no chlorine, no reactive methylene group, and could not be acetylated. Treatment of (II; R′ = H, R″ = CH_2Ph) in ether–dioxan with phosphorus tribromide was shown by Cook *et al.* to give the colourless hydrobromide of 2-benzylthiothiazolone (III). The striking colour of our product showed clearly that compounds of types (I; R = H) and (III) were not present, whilst the ready and rapid formation made it unlikely that very deep-seated changes had occurred. Molecular-weight determinations indicated that two benzylthiothiazolone residues were present, and the compound is suggested as possibly having either the indigo-like structure (IV) or, more probably, the dehydroindigo-like structure (V). Either structure (IV) or (V) would explain the intense colour; whereas (III) and (IV) have the same elemental composition, the formation of (V) would involve oxidation. Treatment with sodium dithionite (hydrosulphite) caused decomposition and the liberation of toluene-ω-thiol due to instability to alkali, but the compound could be reductively acetylated to give a product agreeing in analytical values with the *diacetate* (VI), which might be expected to be formed from either (IV) or (V).

Products of types (IV) and (V) obviously could not be formed from amino-acids other than glycine, as the carbon atoms required to carry the indigoid or dehydroindigoid double bonds would carry a substituent. Moreover an analogue of (V) could not be formed from the corresponding sarcosine derivative, nor could an analogue of (IV) if, as seems probable from the evidence below, the reaction takes place *via* the thiazolone type of structure (III). In agreement with this, treatment of *N*-dithiocarbobenzyloxy-DL-phenylalanine with thionyl chloride gave only a brown gum from which was isolated in low yield pale yellow needles of a compound obviously quite different in type from the highly coloured glycine derivative, nor was any highly coloured material obtained by the action of thionyl chloride on *N*-dithiocarbobenzyloxysarcosine. On the other hand very vigorous reaction occurred when thionyl chloride was added to *N*-dithiocarbocarbethoxyglycine, $EtO_2C\cdot S\cdot CS\cdot NH\cdot CH_2\cdot COOH$ (Cook *et al.*, *loc. cit.*), to yield a highly coloured material, and a similar product was obtained by the action of thionyl chloride on *N*-dithiocarbo-*m*-nitrophenacyloxyglycine, *m*-$NO_2\cdot C_6H_4\cdot CO\cdot CH_2\cdot S\cdot CS\cdot NH\cdot CH_2\cdot COOH$.

The mechanism of the reaction is obscure. When dithiocarbobenzyloxyglycine was treated with oxalyl chloride (cf. Adams and Ulich, *J. Amer. Chem. Soc.*, 1920, **42**, 599) only a yellow gum was obtained, presumably containing the hydrochloride of (III), and, as Cook *et al.* showed, the use of phosphorus tribromide gives the hydrobromide of (III). It was found that on treatment of this hydrobromide with thionyl chloride a vigorous reaction again occurred in the cold, and the product was identical with that from dithiocarbobenzyloxyglycine itself. It is therefore suggested that formation of (IV) or (V) occurs by way of the benzylthiothiazolone (III), possibly with intermediate chlorination and loss of hydrogen chloride between two molecules. An indigoid structure similar to (IV), but formed from two glyoxaline nuclei, has been postulated by Hunter and Hlynka (*Canadian J. Res.*, 1941, **19**, *B*, 305) for a compound which they prepared.

As this is not connected with the main problem in hand further work has not been carried out, but the results are reported in view of the current interest in thiazole chemistry.

Experimental.—Thionyl chloride (10 ml.) was added to *N*-dithiocarbobenzyloxyglycine (10 g.) in a flask protected from moisture. Vigorous evolution of gas occurred and the mixture became deep red. When the initial reaction had subsided the flask was heated for 15 minutes in a water-bath at 40°, and the excess of thionyl chloride then pumped off. The dark residue was recrystallised from benzene and then from dioxan. The *product* formed glistening scarlet needles, m. p. 202° (decomp.). The purified material (3·6 g.) was dried (P_2O_5) for 4 hours at 80° in a high vacuum before analysis; the molecular weight was determined by elevation of the b. p. of benzene [Found: C, 54·4; H, 3·6; N, 6·4; S, 27·8%; *M*, 437 (mean). The dehydroindigoid formula (V), $C_{20}H_{16}O_2N_2S_4$, requires C, 54·0; H, 3·6; N, 6·3; S, 28·8%; *M*, 444. The indigoid formula (IV), $C_{20}H_{18}O_2N_2S_4$, requires C, 53·8; H, 4·0; N, 6·3; S, 28·7%; *M*, 446]. This material (0·5 g.) was reductively acetylated by boiling it for 3 hours with acetic anhydride (5 ml.), acetic acid (5 ml.), and powdered zinc. Almost colourless needles of an *acetate*, m. p. 133—135°, were obtained. These darkened somewhat on exposure to air [Found: C, 54·0; H, 4·7; N, 5·5. The diacetate (VI), $C_{24}H_{24}O_4N_2S_4$, requires C, 54·1; H, 4·5; N, 5·3%].

Treatment of DL-phenylalanine in alkaline solution with carbon disulphide and then benzyl chloride, according to the instructions given by Cook *et al.* for the glycine derivative, gave N-*dithiocarbobenzyloxy*-DL-*phenylalanine*, which could not be induced to crystallise (Found: N, 4·3. $C_{17}H_{17}O_2NS_2$ requires N, 4·2%). Similar treatment of sarcosine gave N-*dithiocarbobenzyloxysarcosine*, as colourless needles, m. p. 119—120°, from ethyl acetate–ligroin (Found: N, 5·3. $C_{11}H_{13}O_2NS_2$ requires N, 5·5%). Treatment of glycine with carbon disulphide and then *m*-nitrophenacyl bromide dissolved in dioxan gave N-*dithiocarbo*-m-*nitrophenacyloxyglycine*, m. p. 141° (decomp.) (from ethyl acetate) (Found: N, 9·0. $C_{11}H_{10}O_5N_2S_2$ requires N, 8·9%).

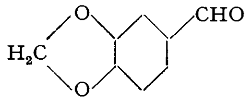
When *N*-dithiocarbobenzyloxy-DL-phenylalanine was treated with thionyl chloride and the excess removed as already described for the glycine analogue, a yellowish mass remained and was purified by precipitation from an ethyl acetate solution by ligroin, followed by recrystallisation. Long (2—3 cm.) straw-coloured needles of a compound, m. p. 119—120°, were obtained (Found: C, 66·7; H, 5·3; N, 5·9%). The action of thionyl chloride on *N*-dithiocarbo-*m*-nitrophenacyloxyglycine gave brick-red needles, which darkened above 180°, decomposed at 201°, and also decomposed in hot solution. *N*-Dithiocarbocarbethoxyglycine gave green irridescent needles, m. p. 218° (decomp.).

The author thanks Professor A. R. Todd, F.R.S. for his interest.—UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, May 16th*, 1949.]

The Dipole Moment of Piperonal and Piperonylideneaniline.

By R. J. W. LE FÈVRE and (MISS) JEAN NORTHCOTT.

IN another connection it became of interest to ascertain whether the methylenedioxy-ring in piperonaldehyde has a significant effect on the resultant molecular polarity of molecules containing it. Accordingly the moments of piperonaldehyde and its anil were determined in benzene solution, using apparatus and techniques already described (Calderbank and Le Fèvre, *J.*, 1948, 1949).



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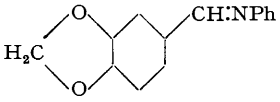

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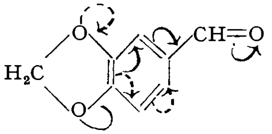

(III.)

Recrystallised piperonaldehyde (from aqueous alcohol) was distilled (b. p. 142°/18 mm.) immediately before use. The anil (cf. Lorenz, *Ber.*, 1881, **14**, 792), after crystallisation from ligroin, had m. p. 65° in agreement with the literature. Experimental data and calculations are tabulated below, using symbols explained in " Dipole Moments " (Methuen, 1948, pp. 39—41):

Dielectric constants and densities.

$10^6 \times w_1$.	$\varepsilon^{25°}$.	d_4^{25}.	$\alpha\varepsilon_2$.	β.
—	2·2725	0·87378	—	—
		Piperonaldehyde.		
3,521	—	0·87487	—	0·356
4,820	—	0·87528	—	0·357
5,219	2·3206	0·87557	9·15	0·389
6,428	2·3329	0·87589	9·40	0·376
6,931	—	0·87593	—	0·354
7,667	2·3416	$0{\cdot}87608_5$	9·01	0·345
8,654	2·3512	0·87631	9·09	0·335
19,739	2·4521	0·87960	9·10	0·337
		Piperonylideneaniline.		
3,344	2·2793	0·87464	2·03	0·295
6,504	2·2856	0·87543	2·01	0·290
8,781	2·2901	0·87605	2·00	0·296
12,721	2·2987	—	2·06	—

Molecular refractions.

$10^6 \times w_1$.	d_4^{25}.	n_D^{25}.	r_{12} (c.c.).	$(R_L)_D$ c.c.
0	0·87378	1·4972 *	$0{\cdot}33500_5$	—
		Piperonaldehyde.		
7,667	$0{\cdot}87608_5$	1·4979 *	0·33442	39·3 †
		Piperonylideneaniline.		
6,504	0·87543	1·4992 *	$0{\cdot}33551_5$	69·9 †

* Abbé refractometer used.

† Calc. from benzaldehyde ($R_D = 32$) or benzylideneaniline ($R_D = 62$) by adding R_O and twice $R_{Ether\cdot O} = 38$ and 68 c.c. respectively. Conduché (*Ann. Chim. Phys.*, 1908, [viii], **13**, 94) found a mean value of 40 c.c. for piperonaldehyde in acetic acid solutions.

Results.

	m.	$\alpha\varepsilon_2$.	β.	P_T.	$[R_L]_D$.	μ_D.
Piperonaldehyde	150·13	9·15	0·356	$291{\cdot}3_5$	39·3	$3{\cdot}4_9$
Piperonylideneaniline	225·24	$2{\cdot}02_5$	0·294	140·0	69·9	$1{\cdot}8_5$

Results.

Discussion.—These appear to be the first dipole-moment determinations of compounds possessing the methylenedioxy-group. Comparisons with benzaldehyde (2·98 D.; Calderbank and Le Fèvre, this vol., p. 1462) and benzylideneaniline ($1{\cdot}6_1$ D.; de Gaouck and Le Fèvre, *J.*, 1938, 741) show the values now recorded to be slightly greater in each case (by μ = 0·5 and 0·3 D., respectively). Since the molecular resultant in benzaldehyde has a direction of action lying at 143½° to an axis set successively through carbon atoms nos. 4 and 1 and has its negative pole directed away from the *Ar*-nucleus (Coomber and Partington, *J.*, 1938, 1444), it is evident that the hetero-ring contributes a small moment in a co-operative sense.

This increment might arise from an unequality of the effects of ring strain on the $C_{Aliphatic}$–O and $C_{Aromatic}$–O link moments. Thus available data (*Trans. Faraday Soc.*, 1934, Appendix) for the polymethylene ethers $(CH_2)_nO$ (n = 2—5), if analysed on the simplest geometrical assumptions regarding intervalency angles and with the same H–C moment throughout, suggest that μ_{C-O} becomes greater as the ring becomes smaller. Walsh (*Ann. Reports*, 1947, 45) has noted that, for a given bond, the stretching force constant and the polarity run somewhat inversely. It may therefore be relevant that for the C–O links in dimethyl ether and ethylene oxide the former property appears as 4·53 or 4·56 and 4·43 × 10^5 dynes/cm., respectively (quoted by Ramsay, *Proc. Roy. Soc.*, 1947, *A*, **190**, 573).

Qualitatively, however, since piperonaldehyde undergoes halogenation and nitration in the 6-position (cf. Beilstein, " Handbuch," *XIX*, 115, for references) we prefer to ascribe the slight increase of moment observed to the mesomerism expressed by (III), which indicates graphically one way in which the C–O bond moment may be modified by the C being " aliphatic " or " aromatic."

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