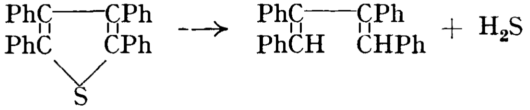
NOTES.

Reduction Experiments with 2 : 3 : 4 : 5-*Tetraphenylthiophen.* By ERNST BERGMANN.

A COMPOUND, m. p. 255°, stated without proof to be $\alpha\beta\gamma\delta$-tetraphenylbutane, was obtained by Baumann and Klett (*Ber.*, 1891, **24**, 3307) by heating stilbene with sulphur and by Fromm and Achert (*Ber.*, 1903, **36**, 539) by the thermal decomposition of dibenzyl sulphide or dibenzyl disulphide or by the reduction of 2 : 3 : 4 : 5-tetraphenylthiophen with zinc and hydrochloric acid. The present author has described (*Annalen*, 1933, **500**, 122) an $\alpha\beta\gamma\delta$-tetraphenylbutane, m. p. 86°. Although two diastereoisomeric forms are theoretically possible, the difference of the m. p.'s seems to be too great. On repetition, no tetraphenylbutane was obtained under the conditions of reduction reported by Fromm and Achert; only on treatment with sodium and amyl alcohol was the tetraphenylthiophen desulphurated and hydrogenated, $\alpha\beta\gamma\delta$-tetraphenylbutane, m. p. 86°, and 1 : 2-diphenyl-3-benzylhydrindene, m. p. 182°, being formed. Both these substances have been obtained (*Annalen, loc. cit.*) by the same treatment of $\alpha\beta\gamma\delta$-tetraphenyl-$\Delta^{\alpha\gamma}$-butadiene. Therefore the conclusion is obvious that the first step in the reduction of tetraphenylthiophen is the conversion into $\alpha\beta\gamma\delta$-tetraphenylbutadiene :



Tetraphenylthiophen (18 g.) was prepared according to Baumann and Klett (*loc. cit.*) from stilbene (30 g.) and sulphur (9 g.) at 240° (6 hours), no higher-melting product being formed. After recrystallisation from amyl alcohol, the product had m. p. 178°. A portion (5 g.) was treated with zinc dust (30 g.) and concentrated hydrochloric acid (50 c.c.) in a boiling mixture of benzene (100 c.c.) and alcohol (40 c.c.) for 4 hours. After cooling, the solid was collected and extracted with boiling benzene, and pure tetraphenylthiophen (m. p. 185°) precipitated with alcohol. Reduction did not occur, even under more drastic conditions.

Reduction. Sodium (7 g.) was introduced in small portions into a boiling solution of tetraphenylthiophen (1·9 g.) in amyl alcohol (100 c.c.), the solution poured into 50% acetic acid, and the 1 : 2-diphenyl-3-benzylhydrindene collected and recrystallised from amyl alcohol; m. p. and mixed m. p. 181—182°. The filtrate was treated with steam, the residue dissolved in ether and dried, the solvent evaporated, and the $\alpha\beta\gamma\delta$-tetraphenylbutane crystallised by trituration with light petroleum; m. p. and mixed m. p. 86°.—THE DANIEL SIEFF RESEARCH INSTITUTE, REHOVOTH, PALESTINE. [*Received, December 9th,* 1935.]

Glucosides of the Glyoxaline Series. By E. BERGMANN and H. HEIMHOLD.

GULLAND and MACRAE (J., 1933, 663) prepared the glucoside of 4-methylglyoxaline from the silver derivative of the latter and tetra-acetobromoglucose. In the same way we have prepared (see Thesis, H. Heimhold, Berlin, 1932) from glyoxaline the crystalline *tetra-acetoglucosido-* and *triacetorhamnosido-glyoxaline* and have deacetylated them in the ordinary way. Tetra-acetogalactosido- and hepta-acetolactosido-glyoxaline were obtained only as syrupy masses. Our substances, too, showed a high resistance against acid hydrolysis, but it has been proved again that they do not contain free imino-groups.

Silver Glyoxaline.—To 14·2 g. of glyoxaline (b. p. 138°/14 mm.; Fargher and Pyman, J., 1919, **115**, 228) in 100 c.c. of water, 39 g. of silver nitrate, dissolved in 120 c.c. of water, and then 78 c.c. of 25% aqueous ammonia, were added. The white precipitate was washed with water, alcohol, and ether and dried. Yield, 31 g. (Found : Ag, 61·4. Calc. for $C_3H_3N_2Ag$: Ag, 61·7%).

N-*Glucosidoglyoxaline.*—The speed of the reaction between silver glyoxaline and acetohalogenoses depends largely on the surface properties of the silver compound. The reaction times given below are the maximal ones; sometimes the reaction finished in a quarter of the time stated.

Silver glyoxaline (2 g.) was heated for 4 hours with tetra-acetobromoglucose (4·1 g.) in 40 c.c. of xylene. *Tetra-acetoglucosidoglyoxaline* (1·5 g.) crystallised from the filtered solution on cooling. Recrystallisation from propyl alcohol gave silky needles, m. p. 205—208° (Found : C, 51·7; H, 5·7; N, 6·3. $C_{17}H_{22}O_9N_2$ requires C, 51·3; H, 5·5; N, 7·0%). 6·05 Mg. gave no methane in the Zerewitinoff apparatus. According to the method of Zemplén and Pacsu (*Ber.*, 1929, **62**, 1613), 0·5 g. of the above compound in 5 c.c. of methyl alcohol was boiled with 2 c.c. of *N*/10-sodium methoxide for 8 minutes and left at 0° over-night; 0·14 g. of *glucosidoglyoxaline* separated as clusters of stout crystals, m. p. 217° after recrystallisation from propyl alcohol. The same compound was obtained when 3 g. of the above acetyl compound in 240 c.c. of methyl alcohol were saturated with gaseous ammonia and left at 0° over-night; after evaporation in a vacuum, the residue was recrystallised from a small amount of 50% alcohol, forming needles (0·5 g.), m. p. 217—218° (Found: C, 46·7; H, 6·3; N, 12·2; active H, 1·4, 1·5. $C_9H_{14}O_5N_2$ requires C, 47·0; H, 6·1; N, 12·2; active H, 1·7%). In 24% sulphuric acid ($l = 1$, $c = 2{\cdot}056\%$), $\alpha_D = 0{\cdot}062°$; $[\alpha]_D + 3{\cdot}02°$.

N-*Rhamnosidoglyoxaline.*—Silver glyoxaline (0·5 g.) and triacetobromorhamnose (1 g.) (Fischer, M. Bergmann, and Rabe, *Ber.*, 1920, **53**, 2371) were heated in 25 c.c. of xylene for 15 minutes; the solution was filtered into 200 c.c. of pure dry light petroleum; the small prismatic crystals of *triacetorhamnosidoglyoxaline* which separated were recrystallised from benzene; m. p. 177—179° (yield, 0·15 g.) (Found: N, 8·3. $C_{15}H_{20}O_7N_2$ requires N, 8·2%).

0·5 G. of the acetyl compound in 13 c.c. of methyl alcohol was heated for 5 minutes with 20 drops of *N*/10-sodium methoxide and kept over-night; the solvent was then evaporated in a vacuum, and the remaining syrup triturated with light petroleum. Recrystallisation from ethyl propionate gave clusters of prismatic needles, m. p. 153—156° (Found: C, 50·5; H, 6·3. $C_9H_{14}O_4N_2$ requires C, 50·5; H, 6·5%).

The experiments were partly carried out at the Friedrich Wilhelm University, Berlin; the Zerewitinoff determinations were made by Dr. Furter, Zurich.—THE DANIEL SIEFF RESEARCH INSTITUTE, REHOVOTH, PALESTINE. [*Received, December 9th*, 1935.]

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s.-*Di*-p-*anisylpinacol.* By CHARLES W. SHOPPEE.

DI-*p*-ANISYL ketone [2 : 4-*dinitrophenylhydrazone*, orange-red laminæ, from ethyl acetate–ethyl alcohol, m. p. 197° (Found: C, 59·7; H, 4·4. $C_{21}H_{18}O_6N_4$ requires C, 59·7; H, 4·3%)] was stirred in warm alcoholic suspension with aluminium foil (etched with 2*N*-sodium hydroxide and amalgamated with ethereal mercuric chloride solution) for 3 hours (compare Cohen, *Rec. trav. chim.*, 1919, **38**, 75), the solution filtered after 12 hours, the residue repeatedly extracted with boiling alcohol, and the combined extracts and filtrate diluted with an equal volume of water. *s.*-Di-*p*-anisylpinacol, collected after 24 hours and crystallised from much hot alcohol (yield, 20%), formed colourless prisms, m. p. 183° (decomp.), giving a deep blue colour with concentrated sulphuric acid (Found: C, 74·3; H, 6·2. Calc. for $C_{30}H_{30}O_6$: C, 74·1; H, 6·2%). The final filtrate when largely diluted gave 4 : 4′-dimethoxybenzhydrol, m. p. 71° (compare Schnackenburg and Scholl, *Ber.*, 1903, **36**, 654).

Examination of the cooled melt, m. p. 115°, of the pinacol yielded only dianisyl ketone, m. p. 143° (Found: C, 74·35; H, 5·9. Calc. for $C_{15}H_{14}O_3$: C, 74·5; H, 5·8%), and 4 : 4′-dimethoxybenzhydrol, mixed m. p. 71°. An equimolecular mixture of these two substances has m. p. 115·5°. The pinacolin was not detected.

Attempts to prepare the pinacol by Bouvet's method (*Bull. Soc. chim.*, 1915, **17**, 209; he gives no experimental details) from anisylmagnesium bromide (4 mols.) and ethyl oxalate produced an oil consisting essentially of the substituted glycollic ester, $(p\text{-OMe}{\cdot}C_6H_4)_2C(OH){\cdot}CO_2Et$. Migita's failure (*Bull. Chem. Soc. Japan*, 1932, **7**, 334) to obtain the pinacol by Gomberg and Bachmann's method (*J. Amer. Chem. Soc.*, 1927, **49**, 236) has been confirmed.

Anisyltrianisylmethyl Ketone.—The pinacol (0·5 g.) was refluxed with glacial acetic acid (5 c.c.) and a trace of iodine for ½ hour, and the cooled solution diluted. The precipitate, twice crystallised from alcohol, formed colourless prisms, m. p. 142°, giving a blue colour with concentrated sulphuric acid (Found: C, 76·8; H, 6·15. Calc. for $C_{30}H_{28}O_5$: C, 76·9; H, 6·0%). The ketone could not be obtained from dianisyl ketone by reduction with glacial acetic acid and zinc dust as stated by Migita (*loc. cit.*). Neither a semicarbazone nor a 2 : 4-dinitrophenylhydrazone could be prepared.

Anisoyldianisylcarbinol.—A solution of anisil (9 g.) in benzene–ether or anisole–ether was added to a Grignard reagent, prepared from magnesium (3·2 g.) and *p*-bromoanisole (25 g.), at 0°. After eventual heating on the steam-bath, the product was decomposed with ice, acidified with 2*N*-sulphuric acid, and extracted with ether. The oil obtained by evaporation crystallised when rubbed with a little methyl alcohol; recrystallisation from ether–ligroin (b. p.

40—60°) and subsequently from methyl alcohol gave *anisoyldianisylcarbinol* in colourless rhombs, m. p. 117·5° (Found : C, 73·3; H, 5·9; OMe, 25·8. $C_{23}H_{22}O_5$ requires C, 73·0; H, 5·9; OMe, 24·6%).—THE UNIVERSITY, LEEDS. [*Received, March* 20*th*, 1936.]

1-*Methylbenzthiazole.* By J. FRASER and F. M. HAMER.

SINCE its first preparation (Hofmann, *Ber.*, 1880, **13**, 21) 1-methylbenzthiazole has been described in the literature as a liquid. In preparing several kilograms of it by Müller's method of treating 2 : 2'-dinitrodiphenyl disulphide with zinc dust, acetic acid, and acetic anhydride (*Z. Farbenind.*, 1906, **5**, 357), we collected the main fraction at 150—151° (uncorr.)/50 mm. On storage in a cold room, it solidified to colourless tabular crystals, m. p. 14°, which were of rectangular outline and showed straight extinction under the microscope.—KODAK LTD., WEALDSTONE, MIDDLESEX. [*Received, March* 10*th*, 1936.]

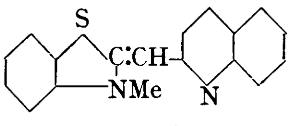
Reactivity of the Imino-group in 1-*Imino*-2-*methylbenzthiazoline.* By LESLIE M. CLARK.

SOME reactions of 2-methylbenzthiazoline (Mills, Clark, and Aeschlimann, J., 1923, **123**, 2353) and of its 1-nitrosoimino-derivative (Besthorn, *Ber.*, 1910, **43**, 1523) have already been recorded. Condensations involving the imino-group of 1-imino-2-methylbenzthiazoline (Besthorn, *loc. cit.*) are now described.

Reaction with Aniline.—This compound (1·6 g.) was boiled with aniline (1·4 g.) for 3½ hours, ammonia being evolved. The oily product crystallised in contact with a little alcohol, and recrystallisation from this solvent (charcoal) gave colourless plates, m. p. 95·5°, of 1-*phenylimino*-2-*methylbenzthiazoline* (Found : C, 69·6; H, 5·0; N, 11·5. $C_{14}H_{12}N_2S$ requires C, 70·0; H, 5·0; N, 11·7%).

Reaction with Phenylthiourea.—The thiourea and the imine in equimolecular proportion were heated at 220° for 4 hours, ammonia being evolved. The product crystallised from alcohol (charcoal) as a mixture of yellow prisms and pale yellow needles. Separation was readily effected, since the needles were considerably less soluble, and the prisms more soluble, in acetone than in alcohol. The prisms, m. p. 184°, were 1-*phenylthiocarbamylimino*-2-*methylbenzthiazoline* (Found : C, 60·2; H, 4·6; N, 13·7; S, 21·4. $C_{15}H_{13}N_3S_2$ requires C, 60·2; H, 4·35; N, 14·0; S, 21·35%). The needles, m. p. 261°, have not been identified (Found : C, 54·9; H, 3·9; N, 14·7; S, 25·8. $C_{17}H_{16}N_4S_2$ requires C, 54·8; H, 4·3; N, 15·0; S, 25·8%).

Reaction with Quinaldine.—1-Imino-2-methylbenzthiazoline (4 g.) was heated with quinaldine (4 g.) at 210° for 8 hours, ammonia being evolved. Volatile base was removed with steam, and addition of hydrochloric acid and alcohol to the dark residue gave a deep reddish-brown solution, from which an impure red monohydrochloride of 2-methylthio-ψ-cyanine crystallised. This was collected and warmed with concentrated hydrochloric acid, giving an almost colourless solution of the dihydrochloride—behaviour typical of the di-acid bases of the cyanine series. The solution was filtered from the comparatively insoluble imino-hydrochloride and basified. Crystallisation from alcohol and ethyl acetate gave 2-*methylthio*-ψ-*cyanine* (annexed formula) in yellow needles, m. p. 165° (Found : C, 74·1; H, 5·2; N, 9·5; S, 11·1. $C_{18}H_{14}N_2S$ requires C, 74·45; H, 4·9; N, 9·7; S, 11·05). The colourless acid solution gave with platinic chloride a pale buff-coloured *platinichloride* (Found : Pt, 27·9. $C_{18}H_{14}N_2S,H_2PtCl_6$ requires Pt, 27·9%.)



No reaction was observed between 1-imino-2-methylbenzthiazoline and α-picoline, acetoacetic ester, or malonic ester at the boiling point, and the evolution of ammonia when the imino-compound was heated with methyl-α- or -β-naphthathiazole at 240° was so slow that the reaction could not be used for synthesising intermediates in the thiocyanine dye series.

When thiourea or phenylthiourea was heated in boiling quinaldine solution, ammonia was evolved, but nothing crystalline was isolated.—WALNUT LANE, HARTFORD, CHESHIRE. [*Received, February* 15*th*, 1936.]
