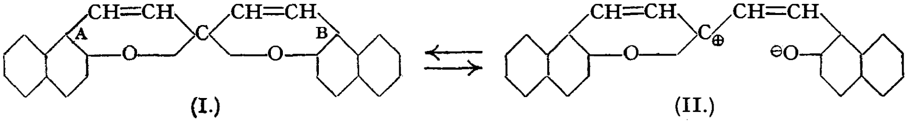
NOTES.

Experiments with Grignard Solutions. Part III. Action of Grignard Solutions on Thermochromic spiro-*Pyrans.* By ALEXANDER SCHÖNBERG, AHMED MUSTAFA, and (in part) (MISS) WAFIA ASKER.

A NUMBER of *spiro*pyrans, *e.g.*, (I), form colourless crystals which give colourless solutions in cold inert solvents, but develop an intense colour, *e.g.*, violet-blue, on heating (Dickinson and Heilbron, *J.*, 1927, 1699) and the process is reversible. This phenomenon has been studied chiefly by Heilbron, Löwenbein, Dilthey and their respective schools and they all agree that the colour change is due to ionic dissociation with the formation of a heteropolar molecule (II).

The *spiro*pyrans showing this colour phenomenon are well crystallised substances, stable to heat and to oxygen; nevertheless, but few physicochemical investigations of the colour phenomenon have been carried out, and the influence of substitution has not been investigated.

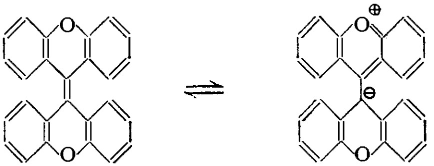
A possible approach to this phenomenon may be to apply the theories used to explain the stability of the free radicals of the triphenylmethyl type. It has been pointed out (see Gilman, "Organic Chemistry," 2nd edtn., p. 1979) that the free radicals formed by dissociation of hexaphenylethane are stabilised by resonance, and it seems possible that this theory may also explain the stability of the zwitterions such as (II). On the other hand, the lowered stability of the spirans (I) may be due to their non-planar configuration (see rings A and B) interfering with the development of resonance.



(I.) Colourless in the cold.

(II.) Violet-blue on heating.

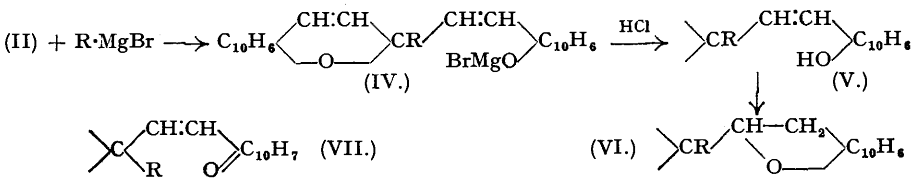
The thermochromic behaviour of the *spiro*pyrans may be related to that of certain ethylenes, *e.g.*, (III*a*) and (III*b*) (Schönberg, Abdel Fattah Ismail, and Asker, *J.*, 1946, 442).



(III*a*.) Colourless in the cold.

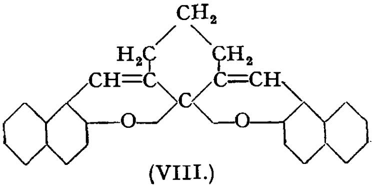
(III*b*.) Bluish-green on heating.

The action of Grignard solutions on the thermochromic *spiro*pyrans has not hitherto been investigated. We have treated *spiro*di-β-naphthopyran (I) with various Grignard solutions, *e.g.*, phenylmagnesium bromide followed by hydrolysis, and find that the reaction leads to formation of 2 : 3-dihydrofuran derivatives (VI) and not of phenolic compounds (V); (VI, R = Ph) is insoluble in aqueous alkali solution, it is not attacked by ethereal diazomethane solution or by benzoyl chloride in the presence of pyridine and is stable towards methyl sulphate in the presence of alkali. These properties make it improbable that the reaction product has the character of an enol or of a potential enol (V or VII). The diene reaction of (VI) with maleic anhydride was negative.

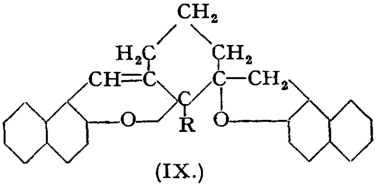


(IV.) (V.) (VI.) (VII.)

Similarly, the action of Grignard solutions on 3 : 3′-trimethylene*spiro*di-β-naphthopyran (VIII) leads to products which show properties analogous to those of (VI, R = Ph). These compounds are therefore formulated as (IX).



(VIII.)



(IX.)

Action of Grignard Reagents on spiro*Di-β-naphthopyran* (I).—(a) *Phenylmagnesium bromide.* To an ethereal solution of phenylmagnesium bromide (magnesium, 0·9 g.; bromobenzene, 9 g.; dry ether, 50 c.c.), the *spiro*pyran (Dickinson and Heilbron, *J.*, 1927, 14; Dilthey and Wizinger, *Ber.*, 1926, **59**, 1856) (2 g.) and dry benzene (20 c.c.) were added. The mixture was refluxed for 2 hours and kept overnight, then decomposed with cold dilute hydrochloric acid and extracted with ether. The ethereal solution was dried and evaporated, and the residue extracted several times with light petroleum (b. p. 30—50°). The petroleum gave, on slow evaporation, colourless crystals which, after repeated crystallisation from petrol (b. p. 100—150°), had m. p. 212—215° (colourless melt). 2-(2′ : 3′-*Dihydro-β-naphthofuran-*2′)-2-*phenyl-β-naphthopyran* (VI, R = Ph) is readily soluble in benzene and xylene but dissolves with difficulty in ligroin. It is insoluble in aqueous sodium hydroxide and dissolves with green fluorescence in concentrated sulphuric acid (Found : C, 87·6; H, 5·2. $C_{31}H_{22}O_2$ requires C, 87·4; H, 5·1%). It is unchanged on further treatment with phenylmagnesium bromide, is not affected by an ethereal solution of diazomethane in the presence or absence of methyl alcohol (cf. Schönberg and Mustafa, *J.*, 1946, **746**), and was unchanged when 0·5 g. was refluxed with maleic anhydride (3 g.) in dry xylene for 6 hours or with pyridine (5 c.c.) containing benzoyl chloride (1·5 g.) for 3 hours. Further, 0·5 g., suspended in methyl alcohol (15 c.c.) and treated first with methyl sulphate (3 c.c.), gradually, and then with methyl-alcoholic potassium hydroxide, was recovered unchanged after 2 hours.

(b) p-*Tolylmagnesium bromide.* The p-*tolyl* analogue was obtained in colourless crystals, m. p. 214°, from alcohol–benzene ; it was insoluble in aqueous sodium hydroxide and slowly gave a red colour when treated with concentrated sulphuric acid [Found : C, 87·4; H, 5·5; *M* (micro-Rast), 412. $C_{32}H_{24}O_2$ requires C, 87·4; H, 5·4%; *M*, 440].

(c) α-*Naphthylmagnesium bromide.* The α-*naphthyl* compound was obtained in colourless crystals, m. p. 260°, from petrol (b. p. 100—150°) ; it was insoluble in aqueous sodium hydroxide, gave a red-brown colouration with concentrated sulphuric acid, and was recovered unchanged or almost so when treated with methyl sulphate (Found : C, 87·8; H, 5·1. $C_{35}H_{24}O_2$ requires C, 88·2; H, 5·0%).

Action of Grignard Reagents on 3 : 3′-*Trimethylene*spiro*di-β-naphthopyran* (VIII).—(a) *Phenylmagnesium bromide.* The *spiro*pyran (Dickinson and Heilbron, *J.*, 1927, 1704; Dilthey and Wübken, *Ber.*, 1928, **61**, 965) was treated as mentioned above. The product was decomposed with dilute hydrochloric acid, extracted with ether, dried, and evaporated. The oily residue was extracted with petrol (b. p. 100—150°) and on slow evaporation gave colourless crystals mixed with an oil. The mixture, on further washing with cold ether, formed a solid which crystallised from petrol (b. p. 100—150°) in colourless crystals, m. p. 238°. 2-(2′ : 3′-*Dihydro-β-naphthofuran-*2′)-2-*phenyl-*2′ : 3-*trimethylene-β-naphthopyran* (IX, R = Ph) dissolves in benzene but is difficultly soluble in hot ethyl alcohol and cold ether and insoluble in aqueous sodium hydroxide. It dissolves with an orange colour in concentrated sulphuric acid (Found : C, 87·6; H, 5·8. $C_{34}H_{26}O_2$ requires C, 87·6; H, 5·6%).

(b) α-*Naphthylmagnesium bromide.* The α-*naphthyl* analogue was obtained in colourless crystals, m. p. 305°, from benzene–petrol (b. p. 100—150°) ; it is insoluble in aqueous sodium hydroxide, dissolves in hot benzene, and with difficulty in petrol, and gives a brownish-red colour in concentrated sulphuric acid (Found : C, 87·9; H, 5·6. $C_{38}H_{28}O_2$ requires C, 88·3; H, 5·4%).—FOUAD I UNIVERSITY, FACULTY OF SCIENCE, CAIRO, EGYPT. [*Received, September* 20*th*, 1946.]

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1 : 1 : 1-*Trichloro-*2 : 2-*di-*(4-ω-*carbomethoxymethoxyphenyl*)*ethane.* By I. E. BALABAN and F. K. SUTCLIFFE.

STEPHENSON and WATERS (*J.*, 1946, 343) describe a compound prepared by the interaction of 4 : 4′-dihydroxy-DT (as disodium salt) with methyl chloroacetate in methanol solution as 4 : 4′-di-(ω-carbomethoxymethoxy)-DT having m. p. 142° (see Errata, 1946). We had previously prepared it by a similar method and found that the dimethyl ester, m. p. 141—143°, was accompanied by a second *substance*, m. p. 82—84°. Stephenson and Waters, however, isolated a single substance, m. p. 142°.

On analysis, both compounds give figures in good agreement for the dimethyl ester, are insoluble in sodium hydrogen carbonate solution, and yield 1 : 1 : 1-*trichloro-*2 : 2-*di-*(4-ω-*carboxymethoxyphenyl*)-*ethane*, m. p. 163—165°, on hydrolysis, identical with the acid prepared from the condensation of phenoxyacetic acid and chloral in the presence of sulphuric acid. The substances, m. p. 82—84° (decomp. 90°), and m. p. 141—143°, are not interconvertible by heating, and the former was recovered unchanged on attempted further esterification on the assumption that it might be the half ester. We are of the opinion, therefore, that they constitute two different forms of the dimethyl ester.

When methyl chloroacetate is brought into reaction with 1 : 1 : 1-trichloro-2 : 2-di-(4-hydroxyphenyl)ethane (as disodium salt) in ethanol solution, *trans*-esterification takes place and the only isolable product is the *diethyl* ester, identical with a specimen prepared from ethyl chloroacetate and the above dihydroxy-compound in ethanol solution. The acid, m. p. 163—165°, esterifies very easily in the presence of a trace of sulphuric acid at ordinary temperature, and consequently, when chloral is condensed with phenoxyacetic acid in the presence of sulphuric acid and the product isolated by the use of methanol, the dimethyl ester and not the free acid is obtained. This was also found to be the case when the dimethyl ester was hydrolysed and worked up in a similar manner.

1 : 1 : 1-*Trichloro-*2 : 2-*di-*(4-ω-*carbomethoxymethoxyphenyl*)*ethane.*—(*a*) A solution of sodium (2·3 g.) in methanol (100 ml.) was added to a solution of 1 : 1 : 1-trichloro-2 : 2-di-(4-hydroxyphenyl)ethane (15·9 g.) in methanol (50 ml.) followed by methyl chloroacetate (16·3 g.). The solution was then heated under reflux for 4—5 hours, during which time salt was deposited and the colour of the solution changed from purple to orange. Most of the methanol was distilled off and the residue steam-distilled to remove excess of methyl chloroacetate. The residual oil was cooled and then shaken with ether; a colourless solid was thus produced. This was collected and recrystallised from methanol and gave 4 g., m. p. 130—136°. Two further recrystallisations from methanol raised the m. p. to 141—143° (yield, 3·1 g.) (Found : C, 51·65; H, 4·24; Cl, 22·68; *M*, 398. Calc. for $C_{20}H_{19}O_6Cl_3$: C, 52·00; H, 4·21; Cl, 23·08%; *M*, 461·5).

The ether solution was washed well with water, dried, and evaporated to give 20 g. of thick, orangecoloured oil which on treatment with methanol gave 10·1 g., m. p. 72—76°. Three recrystallisations from methanol gave 6 g. of material, m. p. 82—84° (Found: C, 52·62; H, 3·91; Cl, 25·60; 23·97%; *M*, 339). No methoxyl was found by the normal method either with this or with the ester, m. p. 141—143°.

(*b*) The reaction was carried out exactly as in (*a*). After the reflux period, the solution was filtered hot to remove salt and then cooled. The crystalline material was collected, washed with a little methanol, dried, and then extracted with water to remove any sodium chloride. There were obtained 5·9 g., m. p. 127—135°. Two more recrystallisations raised the m. p. to 141—143° (yield, 4·5 g.).

The methanol mother-liquor was removed and the residual paste diluted with ether and the inorganic material collected. The ether solution was washed with N/5-sodium hydroxide (3 × 30 ml.), then water, and dried (Na_2SO_4). Evaporation of the ether gave 10·5 g. of residual oil which was taken up in methanol (20 ml.) and left overnight. The solid was collected and recrystallised from methanol to give 3·5 g. of material, m. p. 76—80°. Two further recrystallisations from methanol raised the m. p. to 82—84° (yield, 3·0 g.).

(*c*) The reaction was carried out as above, but with the methanol replaced by an equal volume of ethanol as solvent. The heating period was cut to 2½—3 hours since the separation of salt and disappearance of purple colour took place more rapidly than with methanol as solvent.

The mixture was filtered hot, and on cooling deposited only a further trace of inorganic material. The solvent was removed under reduced pressure and the residual resin (21 g.) dissolved in ether, washed with N/5-sodium hydroxide (3 × 20 ml.) then water, and dried (Na_2SO_4). After removal of the solvent there remained 13·2 g. of resin which was dissolved in ethanol (25 ml.) and allowed to stand. The solid (5·25 g.) was collected and recrystallised thrice from ethanol to give 2·9 g. of microcrystalline powder, m. p. 82—84°, not depressed on admixture with an authentic specimen of the diethyl ester m. p. 82—84°, as prepared below (Found : C, 53·30; H, 4·68; Cl, 23·12. $C_{22}H_{23}O_6Cl_3$ requires C, 53·9; H, 4·70, Cl, 21·76%).

1 : 1 : 1-*Trichloro*-2 : 2-*di*-(4-ω-*carbethoxymethoxyphenyl*)*ethane*.—The reaction was carried out in the same manner as (*c*) above, using sodium (2·3 g.), the dihydroxy-compound (15·9 g.), ethyl chloroacetate (18·4 g.), and ethanol (150 ml.). The amount of the first resin obtained was 20 g., and after washing in ether solution, 12·8 g. This, on treatment with ethanol gave a substance (3·6 g.) which after three recrystallisations from ethanol had m. p. 82—84° (Found : C, 52·97; H, 4·90; Cl, 21·88. Calc. for $C_{22}H_{23}O_6Cl_3$: C, 53·94; H, 4·70; Cl, 21·76%). A mixed m. p. with the substance m. p. 82—84° obtained from (*a*) or (*b*) gave a depression.

1 : 1 : 1-*Trichloro*-2 : 2-*di*-(4-ω-*carboxymethoxyphenyl*)*ethane*.—(i) The dimethyl ester, m. p. 141—143° (5 g.), was heated under reflux with a mixture of glacial acetic acid (40 ml.), water (20 ml.), and sulphuric acid (1 ml.; *d* 1·84) for 2 hours. The mixture was then cooled and diluted with water, and the precipitated resin washed well with water. After being dried in a vacuum at 100°, the resin was stirred with benzene; it then crystallised and was recrystallised from benzene–chloroform (1 : 1) and then benzene. There were obtained 3·9 g. (yield, 84%), m. p. 163—165° (Found : C, 50·48; H, 4·03; Cl, 23·8. $C_{18}H_{15}O_6Cl_3$ requires C, 49·83; H, 3·46; Cl, 24·57%). This substance is readily soluble in sodium hydrogen carbonate solution.

(ii) The substance, m. p. 82—84°, from (*a*) above was hydrolysed exactly as in the previous experiment yielding 2·3 g., m. p. 163—165°, which on admixture with the hydrolysis product of the substance of m. p. 141—143° showed no depression.

(iii) Concentrated sulphuric acid (50 ml.) was added to a well stirred water-cooled mixture of phenoxyacetic acid (33 g.), chloral (14·8 g.), and glacial acetic acid (50 ml.) at such a rate that the temperature of the mixture was kept at 30—40°. The resulting solution was kept overnight at room temperature and then poured into water (1 l.) The deposited resin was well washed by decantation and weighed 34 g. Of this, 10 g. were treated with a mixture of benzene (20 ml.) and chloroform (20 ml.), and set aside; 7 g. of crystals, m. p. 158—160°, separated. Two recrystallisations from benzene gave 5·5 g., m. p. 163—165°, identical with the acid from (i) and (ii).

The remaining 24 g. of resin were treated with methanol (70 ml.) and set aside. The solid (14·2 g.) was collected and recrystallised from acetic acid and then ethanol, and gave the dimethyl ester (9·3 g.), m. p. 143—144°; a mixed m. p. with the compound, m. p. 141—143°, from (*a*) or (*b*) gave no depression.

A solution of the acid (m. p. 163—165°; 0·1 g.) in methanol (1 ml.) containing 0·1% of concentrated sulphuric acid was left at room-temperature for 48 hours. The crystalline material was collected and recrystallised from methanol, yielding 0·08 g. (75%) of fine needles, m. p. 141—143°, not depressed on admixture with the dimethyl ester, m. p. 141—143°, prepared from methyl chloroacetate and the dihydroxy-compound in methanol solution.

The acid (1 g.) in ether (20 ml.) together with four equivs. of diazomethane in ether (20 ml.) was left for two days in the ice-box. The ester which had crystallised was collected, and had m. p. 142° (1 g.). When recrystallised from methanol it had m. p. 143—144° (0·8 g.), not depressed on admixture with the dimethyl ester, m. p. 141—143°.

Analyses and molecular weight determinations are by Drs. Weiler and Strauss.—PHARMACEUTICAL LABORATORY, THE GEIGY COMPANY, LTD., TRAFFORD PARK, MANCHESTER, 17. [*Received, August 15th, 1946.*]

The Preparation of Diethyldithiocarbamato-derivatives of 2 : 2′-Dichlorodiethyl Sulphide.

By R. A. PETERS and R. W. WAKELIN.

THE compounds (I) and II) were prepared under physiological conditions of pH and temperature, since they were used in an enzyme research described elsewhere (Peters and Wakelin, Report to Ministry of Supply, by Peters; No. 72). Previously, Holiday, Ogston, Philpot, Stocken, and Peters (1940)

(Report to Ministry of Supply, No. 17) obtained some non-crystalline products which were used in the research for " mustard gas " antidotes.

$$\underset{\text{(I.)}}{NEt_2\cdot CS\cdot S\cdot CH_2\cdot CH_2\cdot S\cdot CH_2\cdot CH_2Cl} \qquad \underset{\text{(II.)}}{NEt_2\cdot CS\cdot S\cdot CH_2\cdot CH_2\cdot S\cdot CH_2\cdot CH_2\cdot S\cdot CS\cdot NEt_2}$$

2-*Chloroethyl* 2-(N-*Diethyldithiocarbamato*)*ethyl Sulphide* (I).—" Mustard gas " (2 : 2′-dichlorodiethyl sulphide) (2 g.) in ethanol (10 c.c.) was added during 50 minutes with shaking to a solution of sodium diethyldithiocarbamate (6 g., recrystallised from commercial sources) in Ringer phosphate solution (40 c.c.) (pH, 7·3; NaCl, 9 g.; KCl, 0·25 g.; $NaHCO_3$, 0·15 g.; KH_2PO_4, 17·3 g. in 1250 c.c. of water brought to pH 7·35 with 20% NaOH solution) and water (160 c.c.) warmed to 38°. A further small amount of ethyl alcohol (5 c.c.) was used to wash in the remainder of the " mustard gas," and the whole was shaken for 1½ hours at room temperature. The oil was extracted with light petroleum (b. p. 40—60°) and dried (Na_2SO_4). The crude crystals, freed from the light petroleum at the lowest possible temperature, were purified by grinding them with small amounts of absolute ethyl alcohol and filtration upon a sintered glass funnel. Yield of (I), 1·24 g.; 0·5 g. of less pure product (needles) (Found: C, 39·8; H, 6·41; N, 5·1; Cl, 13·1; S, 35·9. $C_9H_{18}NClS_3$ requires C, 39·8; H, 6·63; N, 5·16; Cl, 13·09; S, 35·3%). The *compound* formed platelets from methyl alcohol, m. p. 40·5°.

The compound (I) does not yield chloride ions, and since it does not react with iodine and gives no nitroprusside reaction upon addition of nitroprusside and cyanide, –SH and –S–S groups must be absent, thus confirming the constitution. The rate of formation of hydrochloric acid in 60% ethyl alcohol at 38° for 0·12 ± 0·002M–solutions of " mustard gas " and of (I) (reckoned in terms of Cl content) were substantially the same; *k* is calculated from the total acid formed (Peters and Walker, *Biochem. J.*, 1923, **17**, 160). For 20—50% hydrolysis, $k = 0{\cdot}0109$ (for " mustard gas," $k = 0{\cdot}0104$). This proves that there is still one Cl present from the original " mustard gas."

Longer periods of reaction and shaking gave an impure product melting at 32—33°.

Bis-[2-(N-*Diethyldithiocarbamato*)*ethyl*] *Sulphide* (II).—Crude (I) (1 g.), m. p. 31—35°, was added to a solution of sodium diethyldithiocarbamate (4 g.) in ethyl alcohol (90 c.c.) and water (60 c.c.) and shaken for 2 hours at 38°. The crystals (II) were washed with a small amount of absolute ethyl alcohol and recrystallised from warm ethyl alcohol. The *compound* then had m. p. 65·6° (Found: N, 7·1; Cl, Nil. $C_{14}H_{28}N_2S_5$ requires N, 7·29%). It can also be obtained, as needles, by boiling " mustard gas " (0·5 g.) in ethyl alcohol (40 c.c.) with sodium diethyldithiocarbamate (550 mg.).

Attempts to Prepare the Monohydroxy-compound.—We have tried to make this from the hydrolysate of (I) after warming it with 60% ethyl alcohol as for the determination of *k*. After extraction with light petroleum and evaporation at low temperature we have obtained oils free from chlorine, which have not yet been crystallised.

We are grateful to Dr. E. Holiday for drawing our attention to the presence of impurities in our light petroleum and for the details of purification following Shepard, Henne, and Midgeley (*J. Amer. Chem. Soc.*, 1931, **53**, 1948). We are also grateful to Experimental Station, Porton, for the C and H analysis of (I), and to Dr. L. A. Stocken for advice and for the S analysis. This work forms part of a programme of research carried out for the Ministry of Supply, to whose Chief Scientific Officer we are grateful for permission to publish.—DEPARTMENT OF BIOCHEMISTRY, OXFORD. [*Received, September 5th,* 1946.]

Trityl Derivatives of Xylofuranose : 2-Acetyl 3 : 5-Ditrityl and 2-Methyl 3 : 5-Ditrityl Methylxylofuranoside.

By R. J. MCILROY.

IT has been reported (McIlroy, *J.*, 1946, 100) that acetylation of tritylated methylxylofuranoside (αβ mixture) by acetic anhydride in pyridine before isolation of the trityl derivative yielded a non-crystalline product which analysed as diacetyl monotrityl methylxylofuranoside. It has now been found that acetylation of 3 : 5-ditrityl methylxylofuranoside (isolated) gave solely 2-*acetyl* 3 : 5-*ditrityl methylxylofuranoside*, the properties of which are herein recorded. 2-Methyl 3 : 5-ditrityl methylxylofuranoside, previously reported as a syrup (McIlroy, *loc. cit.*), crystallised after being kept for several months and has been further examined.

2-*Acetyl* 3 : 5-*Ditrityl Methylxylofuranoside.*—To 3 : 5-ditrityl methylxylofuranoside (1·01 g.) dissolved in dry pyridine (10 c.c.) was added acetic anhydride (15 c.c.). After being kept for 24 hours at room temperature, the solution was poured into well stirred ice-water (500 c.c.). The crystalline precipitate which separated was filtered off, washed thoroughly with water, and dissolved in ether, and the ethereal solution was washed thrice with dilute sodium bicarbonate solution, then with water, and dried (Na_2SO_4). Evaporation of the ether yielded colourless crystals of 2-*acetyl* 3 : 5-*ditrityl methylxylofuranoside* (0·95 g.), which after being recrystallised from ethyl alcohol had m. p. 79—79·5°, $[\alpha]_D^{17^\circ}$ + 2·0° in chloroform (*c*, 0·98) (Found: trityl, 70·0; acetyl, 18·5. $C_{46}H_{42}O_6$ requires trityl, 70·4; acetyl, 8·6%).

Deacetylation by methyl alcoholic ammonia at 0° gave 3 : 5-ditrityl methylxylofuranoside, m. p. 77—77·5° alone or admixture with an authentic specimen.

2-*Methyl* 3 : 5-*Ditrityl Methylxylofuranoside* (McIlroy, *loc. cit.*).—This slowly crystallised after being left in contact with alcohol for some months. After being recrystallised from alcohol it had m. p. 80°, $[\alpha]_D^{16^\circ}$ + 1·6° in chloroform (*c*, 0·96) (Found: OMe, 9·2; trityl, 73·3. Calc. for $C_{45}H_{42}O_5$: OMe, 9·4; trityl, 73·4%).

It is interesting to note that there is very little difference between the melting points and the specific rotations of 3 : 5-ditrityl, 2-methyl 3 : 5-ditrityl, and 2-acetyl 3 : 5-ditrityl methylxylofuranoside. Moreover there is no marked depression of m. p. when either the 2-methyl or the 2-acetyl derivative is mixed with 3 : 5-ditrityl methylxylofuranoside.—CANTERBURY UNIVERSITY COLLEGE, CHRISTCHURCH, N.Z. [*Received, September 5th,* 1946.]

Reduction of αβ-Unsaturated Carbonyl Compounds by Sodium Butoxide. By CH. WEIZMANN, M. SULZBACHER, and E. BERGMANN.

MASTAGLI (*Ann. Chim.*, 1938, **10**, 281; Thesis, Paris, 1938; Mastagli, Charrein, and Lambert, *Compt. rend.*, 1945, **221**, 749) has shown that αβ-unsaturated aldehydes and ketones are reduced to the corresponding saturated alcohols by a boiling benzyl-alcoholic solution of potassium hydroxide; α-alkylcinnamaldehydes give *via* the α-alkylcinnamyl alcohols the 3-phenyl-2-alkylpropanols, and phenyl styryl ketone gives, *via* phenyl 2-phenylethyl ketone, 1 : 3-diphenyl-1-propanol. An equivalent amount of benzyl alcohol is oxidised to benzoic acid.

The same mechanism has been proposed for the Guerbet reaction of butyl alcohol (Weizmann, Bergmann, and Haskelberg, *Chem. and Ind.*, 1937, **56**, 587) for which it was assumed that butaldehyde is formed and " crotonised " to 2-ethyl-2-hexenal which is then reduced to 2-ethylhexanol.

It is desired to record some supporting experiments which were carried out in this laboratory some time ago. Isolated 2-ethyl-2-hexenal is, indeed, reduced to 2-ethylhexanol, and benzylideneacetone to 4-phenyl-2-butanol.

Experimental.—(*a*) 2-Ethyl-2-hexenal (b. p. 65—66°/14 mm; 63·0 g., 0·5 mol.) was added to a solution of sodium (11·5 g., 0·5 mol.) in butanol (74 g.). The mixture was heated at 310° for 7 hours; the pressure reached 50 atm.

Acidic products : Butyric acid, b. p. 63—65°/12 mm. (32 g.); 1-ethylpentane-1-carboxylic acid, b. p. 125—127°/16 mm. (5·0 g.). Neutral products : Butanol (20·7 g., 0·28 mol.); aldehyde C_8 (6·0 g., 0·05 mol.); 2-ethylhexanol (53·0 g., 0·40 mol.).

The aldehyde was not separated from the 2-ethylhexanol, but determined in the mixture by titration with hydroxylamine hydrochloride. A high-boiling fraction (190—240°, 15·0 g.) contained esters and an unsaturated aldehyde, possibly identical with the substance $C_{12}H_{22}O_2$ or $C_{12}H_{20}O$, observed by Weizmann and Garrard (*J.*, 1920, **117**, 329) and Batalin and Slawina (*J. Gen. Chem. Russia*, 1937, **7**, 202).

The amount of 2-ethylhexanol formed (0·40 mol.) corresponds well with that of the acid (total 0·43 mol.). If the aldehyde C_8 is assumed to be the starting material, 9·5% of the latter would have escaped reduction. It is not impossible that the (unsaturated) aldehyde fraction contained some 2-ethylhexanal; but this would be in contradistinction to Mastagli's observations on α-alkylcinnamic aldehydes.

(*b*) A solution of sodium (11·5 g., 0·5 mol.) in butanol (74 g.) was heated with benzylideneacetone (m. p. 42°; 73·0 g., 0·5 mol.) at 300° for 6 hours. The acidic product of the reaction consisted of butyric acid (36·0 g.) and 1-ethylpentane-1-carboxylic acid (2·5 g.), *i.e.*, 0·44 mol. (calculated as butyric acid).

From the neutral product were isolated by means of a Widmer column : Butanol (33·0 g., 0·45 mol.); 2-ethylhexanol (5·2 g., 0·04 mol.); 4-phenyl-2-butanol (22·5 g., 0·15 mol.); benzylideneacetone (5·0 g., 0·034 mol.).

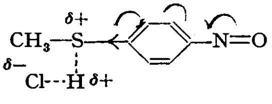
The resinous residue boiled above 200° under 16 mm. pressure.

The 4-phenyl-2-butanol boiled at 115—117°/13 mm. and was identified through its phenylurethane, m. p. 116—117°.

Corresponding to the 0·04 mol. of 2-ethylhexanol formed from butyl alcohol, only 0·04 mol. of butyric acid should have been obtained (Guerbet reaction). Approximately 0·40 mol. of butyric acid was formed, therefore, in the reduction of the unsaturated ketones. The yield of 4-phenyl-2-butanol should also have been 0·40 mol. (Found : 0·15 mol.); the resin formation accounts for the balance.—GROSVENOR LABORATORY, LONDON, S.W.1. [*Received, September 30th*, 1946.]

The Preparation and Some Reactions of 4-Nitrosothioanisole. By HERBERT H. HODGSON, DOUGLAS D. R. SIBBALD, and ERNEST W. SMITH.

THE 3-halogeno-4-nitrosoanisoles had previously been found to lose their methyl groups on keeping, or on heating under reflux with dilute mineral acids, and to be converted into the 3-halogenobenzoquinone 4-oximes (Hodgson and Kershaw, *J.*, 1930, 1969). Similarly, a solution of 3-fluoro-4-nitrosoanisole in methyl alcohol was found to be rapidly converted into 3-fluoro-4-nitrosophenol when shaken with concentrated hydrochloric acid (Hodgson and Nicholson, *J.*, 1940, 1268). It was hoped, therefore, that similar treatment of 4-*nitrosothioanisole* would afford either 4-nitrosophenylthiol or benzothioquinone 4-oxime; instead, however, the methylthio-group resisted disruption, while the nitroso-group was reduced with formation of 4 : 4′-*dimethylthioazoxybenzene*. The latter was also synthesised by condensation of 4-*hydroxyaminothioanisole* with 4-nitrosothioanisole. This reduction of the nitroso-group by only methyl alcohol in the presence of hydrogen chloride is noteworthy, and must be ascribed to recession of electrons from the nitroso-group caused by the methylthio-group, which in turn must be due to incipient salt formation at it, whereby the anionoid character of the methylthio-group is transformed into the kationoid character of the incipient sulphonium group (see inset) (cf. Hodgson and R. Smith, *J.*, 1937, 1634, for salt formation at the phenylthio-group).



Experimental.—*Preparation of* 4-*hydroxyaminothioanisole.* 4-Nitrothioanisole (4 g.), dissolved in ethyl alcohol (15 c.c.), was stirred with a solution of ammonium chloride (0·5 g.) in water (12 c.c.), and the mixture heated until the finely divided suspension of the thioanisole had melted; zinc dust (*ca.* 5 g.) was then added in small portions with vigorous agitation until the supernatant liquor was almost colourless. After hot filtration and washing of the residue with hot ethyl alcohol (15 c.c.), the combined filtrate and washings were chilled by external ice, the light orange separation of crude solid 4-*hydroxyaminothioanisole* filtered off, and washed with a little cold benzene until colourless, minute amounts of azo- and azoxy-compounds being thereby removed; it crystallised from aqueous 50% ethyl alcohol in colourless, iridescent plates, m. p. 85° (to a red liquid with subsequent decomposition) (Found : N, 9·2; S, 20·8. C_7H_9ONS requires N, 9·0; S, 20·6%), which gave a crimson-magenta colour with concentrated sulphuric acid, changing to a blue-violet on heating, and to light yellow on dilution with water.

4-*Nitrosothioanisole* was obtained when a solution of 4-hydroxyaminothioanisole (0·8 g.) in ethyl alcohol (10 c.c.) was added gradually at 0° to a well-stirred solution of anhydrous ferric chloride (3 g.) in water (7 c.c.) containing floating ice; it separated in green crystals which melted below room temperature (Found: N, 9·3; S, 21·1. C_7H_7ONS requires N, 9·15; S, 20·9%) and were volatile in steam. 4 : 4′-*Dimethylthioazoxybenzene* resulted when solutions of equivalent quantities of 4-hydroxyaminothioanisole and 4-nitrosothioanisole in methyl alcohol were mixed together; it crystallised from methyl alcohol in pale yellow micro-needles, m. p. 133° (Found: N, 9·9; S, 22·3. $C_{14}H_{14}ON_2S_2$ requires N, 9·65; S, 22·1%), which gave a magenta-violet colour with concentrated sulphuric acid changing to violet on heating, and, on dilution with water, first to blue and then to yellow.

Action of hydrogen chloride on 4-*nitrosothioanisole.* Dry hydrogen chloride was passed into a solution of 4-nitrosothioanisole in methyl alcohol for 1 hour; the solution became red and deposited iridescent colourless plates of 4 : 4′-dimethylthioazoxybenzene, m. p. and mixed m. p. with authentic specimen above, 133° (Found: N, 9·8; S, 22·2%).

The authors thank Imperial Chemical Industries Ltd., Dyestuffs Division, for gifts of chemicals.—TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, October 2nd*, 1946.]