

NOTES.

Miscellaneous Sulphones. By K. BOWDEN and C. H. REECE.

DURING recent investigations certain sulphones were required as intermediates. As three of these were new, and the known compounds were prepared by improved methods, it seems desirable to record the following data.

4-Nitro-4'-acetamidodiphenyl Sulphone.—4-Nitro-4'-acetamidodiphenyl sulphide (63 g.) was dissolved in glacial acetic acid (250 c.c.) and cooled to 90°. Hydrogen peroxide (95 c.c. of "100-vol.") was added during 45 minutes with stirring under reflux and the mixture then boiled for a further 30 minutes. On cooling, the sulphone (70 g., 100%), m. p. 224°, crystallised. Raiziss *et al.* (*J. Amer. Chem. Soc.*, 1939, **61**, 2763) obtained the sulphone in 81% yield by a rather cumbersome method using potassium dichromate and sulphuric acid.

4 : 4'-Diacetamidodiphenyl Sulphone.—This was similarly prepared (yield, 73%) from 4 : 4'-diacetamidodiphenyl sulphide and had m. p. 282°. Raiziss *et al.* (*loc. cit.*) record a 63% yield.

4-Acetamido-4'-hydrazinodiphenyl Sulphone.—To concentrated sulphuric acid (200 c.c.) at 0° was slowly added sodium nitrite (16 g.) with stirring. The mixture was then carefully warmed to 50°, held at this temperature until all the sodium nitrite had dissolved, and again cooled to 0°. 4-Amino-4'-acetamidodiphenyl sulphide (38 g.) was then added during 45 minutes and stirring continued for a further 15 minutes, after which acetic acid (50 c.c.) was added dropwise at <10° and the mixture stirred for 2 hours at this temperature. The solution was poured on ice (500 g.), and excess nitrous acid destroyed with urea. The diazonium solution so obtained was reduced by adding it to a solution of stannous chloride (150 g.) in concentrated hydrochloric acid (300 c.c.) cooled to 5°. The resultant precipitate, after being crystallised from hot water (300 c.c.), was dissolved in water (500 c.c.) and converted into the free *hydrazine* with aqueous ammonia. The compound crystallised from alcohol as yellow needles, m. p. 210° (4 g., 10%) (Found: C, 55.2; H, 5.0; N, 13.0. $C_{14}H_{18}O_2N_4S$ requires C, 55.1; H, 5.0; N, 13.7%).

4 : 4'-Dihydrazinodiphenyl Sulphone.—4 : 4'-Diaminodiphenyl sulphide (20 g.) was dissolved in concentrated hydrochloric acid (40 c.c.) and water (60 c.c.) and the hot solution poured on ice (100 g.) to precipitate the hydrochloride. This mixture was cooled to 0° and sodium nitrite (15 g.) in water (50 c.c.) added dropwise with stirring during 30 minutes, the temperature being kept below 10°. The solution was then stirred below 10° for 1 hour and excess of nitrous acid destroyed with urea. Reduction was effected by slowly adding the solution to stannous chloride (85 g.) in concentrated hydrochloric acid (170 c.c.) at 5°. The resulting precipitate was crystallised from dilute hydrochloric acid and converted into the free *hydrazine* with aqueous ammonia. The compound crystallised from water as colourless needles, m. p. 190° (slight decomp.) (8 g., 36%) (Found: C, 52.1; H, 5.1; N, 19.3. $C_{12}H_{14}O_2N_4S$ requires C, 51.8; H, 5.1; N, 20.1%).

The dihydrazine (5 g.) in glacial acetic acid (15 c.c.) and water (15 c.c.) was cooled to 10° and a solution of acetone (4 c.c.) in water (6 c.c.) added with stirring. After a further 30 minutes' stirring the precipitated *diisopropylidene* derivative was filtered off, and crystallised from alcohol as bright yellow needles, m. p. 232° (decomp.) (Found: C, 59.6; H, 6.2; N, 14.8. $C_{18}H_{22}O_2N_4S$ requires C, 60.3; H, 6.2; N, 15.6%).—THE UNIVERSITY, LEEDS, 2. [Received, May 5th, 1950.]

The Determination of Fluorine in Organic Compounds. By J. F. ELLIS and W. K. R. MUSGRAVE.

IN adapting Willard and Winter's titration of fluoride by thorium nitrate (*Ind. Eng. Chem. Anal.*, 1933, **5**, 7) to the determination of fluorine in organic compounds, Musgrave and Smith (with Tatlow, *J.*, 1949, 3026) achieved a reproducible end point by filtering off the bulk of the thorium fluoride before completing the titration. In addition, the observation by Stross (*Metallurgia*, 1947, **36**, 346) and Milton *et al.* (*Analyst*, 1947, **72**, 43) that the introduction of starch prevents the precipitation of thorium fluoride and so eliminates the necessity for the filtration, was confirmed by one of us (W. K. R. M.). Neither Stross nor Milton *et al.* gave details, and it has been found that in the presence of the products of fusion of an organic compound certain precautions have to be taken. The following method has now been found satisfactory.

To an aliquot containing not more than 10 mg. of fluoride ion, add 1 ml. of 0.05% aqueous sodium alizarinsulphonate and discharge any purple colour by dropwise addition of 2N-nitric acid. Add 5 ml. of half-neutralised chloroacetic acid as buffer and 5 ml. of 5% starch solution (previously filtered through Whatman No. 3 paper). Dilute the solution to 100 ml. and titrate it with 0.05N-thorium nitrate solution. At the end-point the colour in the solution changes from pale yellow to pink.

It is essential to use freshly prepared starch solution for its efficacy is lost after about 12 hours. Further, its action as a protective colloid for thorium fluoride is not indefinite in duration and this is precipitated if the titration is not completed quickly, preferably within one minute.

In applying this method to solutions containing alcohol and sodium cyanide, hydroxide, chloride, and sulphide, it was found that the first two have to be removed (see Table I). The alcohol, which causes premature precipitation of thorium fluoride, is eliminated by evaporating the solution to one-tenth of its volume, adding water, and repeating the evaporation. The cyanide ion, which depresses the end-point slightly, is removed by precipitation from the slightly acid (HNO_3) solution by adding a slight excess of N-silver nitrate. The excess of silver ion is removed by adding a little N-sodium chloride so as to prevent reaction with the buffer, and the precipitates are filtered off on a No. 40 paper after coagulation at 70°. Sulphide ion, if present, is precipitated with the silver cyanide and chloride in a very fine state which passes through the filter, and the precipitate, in this case, must be removed by centrifuging and decantation through a No. 40 filter.

TABLE I.

(All solutions contained 25 ml. of 0.1035N-NaF in 500 ml.; 50-ml. aliquots were taken.)

Additional: ml. of n-soln.	Th(NO ₃) ₄ , N.	Vol. of Th(NO ₃) ₄ :	
		found.	calc.
NaOH, 60	0.0474	5.46, 5.46 *	5.46
,, 60; NaCN, 10	0.0474	5.43, 5.43	5.46
,, 50; ,, 5	0.0419	6.15, 6.15	6.18
,, 50; ,, 2	0.0419	6.16, 6.16	6.18
,, 50; NaCl, 2	0.0419	6.18, 6.18	6.18
,, 50; ,, 10	0.0419	6.18, 6.18	6.18
,, 50; ,, 20	0.0419	6.18, 6.18	6.18
,, 60; Na ₂ S, 10	0.0474	5.46, 5.46	5.46

* When the solution used in this titration contained 50% of alcohol, 5.25 ml. of 0.0474N-Th(NO₃)₄ were required (calc.: 5.46 ml.) and the end-point was obscure.

After removal of the interfering ions the buffer and starch solutions are added (the indicator and nitric acid having been added previously), and the solutions made up to 100 ml. and titrated with thorium nitrate. As a result the titration figures are restored to the correct values.

Application of the method to organic compounds gave the results shown in Table II. The fusions were carried out upon 50—100 mg. of the compound in a nickel bomb. The fusion solution was made up to 100 ml. after removal of the alcohol, and an aliquot containing about 5 mg. of fluoride ion was taken. If only a small quantity of the compound was available, 15—20 mg. were used and the whole of the fusion solution was used in one titration.

TABLE II.

[0.0419N-Th(NO₃)₄ was used except for the determination denoted by an asterisk, for which 0.0474N-Th(NO₃)₄ was used.]

Compound.	Wt. of sample (g.).	Vol. of Th(NO ₃) ₄ (ml.).	F, %:	
			found.	calc.
C ₇ F ₁₄	0.01562	2.98, 2.99	75.8	76.0
C ₂ F ₂ Cl ₄	0.05082	2.38, 2.38	18.6	18.62
C ₂ F ₃ Cl ₃	0.01847	1.40, 1.40	30.2	30.4
	0.05303	4.07, 4.06	30.3	30.4
C ₇ H ₅ O ₂ N ₂ F ₃	0.10030 *	6.14, 6.14	27.5	27.65
	0.06995	4.84, 4.83	27.55	27.65
	0.09674	6.68, 6.70	27.5	27.65
C ₁₁ H ₉ O ₂ NCIF ₃	0.07792	3.98, 4.00	20.40	20.40
	0.07576	3.85, 3.84	20.25	20.40
	0.02158	5.47	20.25	20.40
C ₉ H ₃ O ₄ NSF ₃	0.08454	4.26, 4.26	20.0	20.10
	0.08918	4.48, 4.48	19.95	20.10
	0.08078	4.06, 4.07	20.0	20.10

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The Double Salts, Sodium Cobalt Sulphate and Sodium Magnesium Sulphate. By HENRY BASSETT and (the late) JOSEPH H. HENSHALL.

THE following experiments were carried out some years ago in an endeavour to throw further light on the conditions under which replacement of M''(H₂O)₄ by Na₂(H₂O)₂ in hydrated salts appears to be possible. The most striking instances of this type of replacement had been found in the systems NaCl-NiCl₂-CdCl₂-H₂O and NaCl-CoCl₂-CdCl₂-H₂O (Bassett, Henshall, Sergeant, and Shipley, *J.*, 1933, 646).

A complete explanation of the phenomena can only be expected from an X-ray study of the double salts concerned, but this is not available and offers difficulties. Isomorphous replacement by cations of different valency associated with compensatory changes in hydration has been established in certain cases, notably for the alunites and jarosites (Hendricks, *Amer. Min.*, 1937, 22, 772; Bassett and Goodwin, *J.*, 1949, 2253).

Since the well-known double sulphates Na₂SO₄.M''SO₄.4H₂O may contain an ion [M''(H₂O)₄]' it seemed possible that careful examination of such compounds might show that their composition was somewhat variable owing to some replacement of the type mentioned above. Much phase-rule work has been carried out on the compounds of this group but the information available in the literature on the point under discussion is scanty and somewhat contradictory. In many cases the double salts have only been analysed after crystallisation from solutions containing the constituents in equimolecular proportions, while in several examinations of the ternary systems Na₂SO₄-M''SO₄-H₂O the solid phases have been identified merely from the appearance of the crystals. Schreinemaker's method of residues involving analyses of the moist solid phases is essential for deciding whether any variation in composition of the double salt occurs over the range of solutions with which it can be in equilibrium. Archibald and Gale (*J. Amer. Chem. Soc.*, 1924, 46, 1760) made a complete examination of this nature of the system Na₂SO₄-MgSO₄-H₂O at 40° and 50°, and their results show that the double salt (astrakanite, Na₂SO₄.MgSO₄.4H₂O) has a fixed composition.

Benrath and Cremers (*Z. anorg. Chem.*, 1930, **189**, 86) examined the system $\text{Na}_2\text{SO}_4\text{-ZnSO}_4\text{-H}_2\text{O}$ at 80° and found a fixed composition for the double salt $\text{Na}_2\text{SO}_4\cdot\text{ZnSO}_4\cdot 4\text{H}_2\text{O}$. Benrath's figures for the corresponding nickel system (*ibid.*, 1931, **202**, 161) suggest that the composition of the double salt $\text{Na}_2\text{SO}_4\cdot\text{NiSO}_4\cdot 4\text{H}_2\text{O}$ at 60° may be variable, while the only available data for the cobalt system (contained in the same paper) give two tie-lines for the system $\text{Na}_2\text{SO}_4\text{-CoSO}_4\text{-H}_2\text{O}$ at 60° , which are inconclusive and intersect at some distance from the point for $\text{Na}_2\text{SO}_4\cdot\text{CoSO}_4\cdot 4\text{H}_2\text{O}$.

We examined the system $\text{Na}_2\text{SO}_4\text{-CoSO}_4\text{-H}_2\text{O}$ at 25° , using iron- and nickel-free cobalt sulphate, with all the usual precautions. Cobalt was weighed as Co_3O_4 after precipitation with 1-nitroso-2-naphthol; sulphate was determined by the standard method as BaSO_4 ; and the value for Na_2SO_4 was obtained by calculation. The results are given in the Table.

Solution.		Moist solid.		Nature of solid.
CoSO_4 , %.	Na_2SO_4 , %.	CoSO_4 , %.	Na_2SO_4 , %.	
—	21.80	—	—	$\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$
5.50	21.05	0.55	41.18	"
9.66	20.13	0.86	42.13	"
12.19	20.06	5.31	39.95	$\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4\cdot\text{CoSO}_4\cdot 4\text{H}_2\text{O}$
14.14	19.37	3.76	38.07	$\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$ (metastable)
13.25	18.68	35.53	33.25	$\text{Na}_2\text{SO}_4\cdot\text{CoSO}_4\cdot 4\text{H}_2\text{O}$
13.80	17.98	36.22	34.15	"
15.90	16.05	36.46	33.59	"
19.70	12.85	38.83	34.58	"
22.78	10.51	39.55	34.40	"
23.30	10.68	37.72	32.05	"
23.40	10.53	43.08	22.00	$\text{Na}_2\text{SO}_4\cdot\text{CoSO}_4\cdot 4\text{H}_2\text{O}$ and $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$
24.72	7.41	52.15	0.65	$\text{CoSO}_4\cdot 7\text{H}_2\text{O}$
25.90	4.39	52.78	0.64	"
26.05	2.85	52.65	0.30 *	"
27.33	—	—	—	"

* Direct determination.

The lines for the double salt all run exactly to the point corresponding to $\text{Na}_2\text{SO}_4\cdot\text{CoSO}_4\cdot 4\text{H}_2\text{O}$.

Caven and Gardener who had previously examined the cobalt system at 25° (*J.*, 1933, 943) made no analysis of solid phases. Their solubility curves agree well with ours, apart from the fact that their Na_2SO_4 -double-salt point and the succeeding double-salt point appear to represent considerably supersaturated conditions. They give for the mixture point, CoSO_4 , 15.29; Na_2SO_4 , 19.40%.

We also re-examined the double-salt region of the 25° isotherm of the $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$ system and fully confirmed the results of Archibald and Gale (*loc. cit.*). We determined sodium by the zinc uranyl acetate method, as well as magnesium and sulphate, and the direct results for sodium agreed excellently with those calculated from the magnesium and sulphate determinations.

The new evidence for $\text{Na}_2\text{SO}_4\cdot\text{CoSO}_4\cdot 4\text{H}_2\text{O}$, taken in conjunction with the results previously referred to for the corresponding magnesium and zinc salts, makes it highly probable that none of the double salts of this series has a variable composition.—THE UNIVERSITY, READING. [Received, March 29th, 1950.]

The Reaction of Phenols with Phenyl and 1-Naphthyl isocyanate. By J. M. LYONS and R. H. THOMSON.

THE value of 1-naphthyl isocyanate as a general reagent for the characterisation of phenols was first demonstrated by French and Wirtel (*J. Amer. Chem. Soc.*, 1926, **48**, 1736). These workers prepared some thirty 1-naphthylurethanes but they stated that polyhydric phenols, particularly catechol, resorcinol, quinol, and pyrogallol, did not react with 1-naphthyl isocyanate. This is true only in the absence of a catalyst, since we find that reaction takes place readily in the presence of triethylamine (the catalyst which French and Wirtel recommended). The poly-1-naphthylurethanes have now been obtained by either heating the phenols with a slight excess of 1-naphthyl isocyanate in boiling light petroleum (b. p. $100\text{--}120^\circ$) containing a drop of triethylamine for 20 minutes, or mixing the phenol and reagent in a dry test-tube and stirring with a glass rod previously dipped in triethylamine. The latter method is less suitable in most cases as the mixture usually solidifies so rapidly that effective stirring is not possible, and there is a tendency for isocyanates to dimerise in contact with triethylamine. A number of new poly-1-naphthylurethanes and bisphenylurethanes are detailed below. Many of these derivatives are difficult to crystallise and some show unsatisfactory melting-points; in general they are not suitable for the characterisation of polyhydric phenols.

The failure of a number of monohydric phenols to form phenylurethanes is recorded in the literature. These include 2 : 6-diacetyl-3 : 5-dimethylphenol and various 4-substituted-2 : 6-di-*tert.*-butylphenols (McKinley, Nickels, and Sidhu, *Ind. Eng. Chem. Anal.*, 1944, **16**, 304), 2 : 4-dinitrophenol, 4-chloro-2 : 6-dinitrophenol, and picric acid (Tarbell, Mallatt, and Wilson, *J. Amer. Chem. Soc.*, 1942, **64**, 2229). The failure of juglone to react with phenyl isocyanate has been reported by one of us (*J.*, 1950, 1737), and we now find that the *peri*hydroxyquinones, naphthazarin, 1 : 5- and 1 : 8-dihydroxyanthraquinone behave in the same way. This phenomenon has been attributed previously to the presence of negative groups, or to steric hindrance, but it may be observed that all the compounds mentioned above, with the exception of the 2 : 6-di-*tert.*-butylphenols, contain intra-molecular hydrogen bonds. It is well known that increasing acidity of the hydroxyl group, which would be promoted by the introduction of negative groups into the nucleus, increases the tendency to form hydrogen bonds, and this would explain why 2 : 4-dinitrophenol does not react with phenyl isocyanate under any conditions whereas *o*-nitrophenol

does, although with difficulty ["Organic Reagents for Organic Analysis," Hopkin and Williams Ltd., London, 1944, p. 76; cf. McKinley *et al. (loc. cit.)*]. The reluctance of *o*-hydroxyazo-compounds to react with this reagent is also ascribed to hydrogen-bond formation (Hunter, *Ann. Reports*, 1946, **43**, 146) and it seems likely that the inability of some phenols to form urethanes is due in part to their hydrogen-bond structure, although steric considerations are obviously important in certain cases. However in such compounds as salicylaldehyde and methyl salicylate, the hydrogen bonds are not strong enough to suppress the normal reactivity of the hydroxyl group, and these compounds form phenylurethanes.

1-Naphthylurethanes.—*Catechol*, needles (from ethyl acetate), m. p. 174–175° (this compound melts and resolidifies immediately, finally decomposing at ca. 295°) (Found: C, 75.3; H, 4.5; N, 6.5; $C_{22}H_{20}O_4N_2$ requires C, 75.0; H, 4.5; N, 6.25%). *Resorcinol*, needles, m. p. 206° (from aqueous dioxan) (Found: C, 75.0; H, 4.5; N, 6.05%). *Quinol*, micro-crystals, m. p. 247°, from anisole (Found: C, 75.1; H, 4.7; N, 6.0%). *Pyrogallol*, micro-crystals (from glacial acetic acid), m. p. 181° (melts and resolidifies immediately, finally decomposing at ca. 270°) (Found: C, 74.0; H, 4.45; N, 6.3. $C_{29}H_{27}O_6N_3$ requires C, 73.9; H, 4.3; N, 6.6%). **1:4-Dihydroxynaphthalene**, leaflets, m. p. 220° (from aqueous dioxan) (Found: C, 77.3; H, 4.7; N, 5.3. $C_{22}H_{22}O_4N_2$ requires C, 77.1; H, 4.45; N, 5.6%). **1:5-Dihydroxynaphthalene**, needles, m. p. 240°, from aqueous dioxan (Found: C, 77.3; H, 4.6; N, 5.75%). **1:7-Dihydroxynaphthalene**, micro-crystals, m. p. 185°, from aqueous acetic acid (Found: C, 77.3; H, 4.6; N, 5.8%). **1:8-Dihydroxynaphthalene**, leaflets, m. p. 220°, from aqueous acetic acid (Found: C, 77.1; H, 4.7; N, 5.8%).

Phenylurethanes.—**1:5-Dihydroxynaphthalene**, leaflets (from glacial acetic acid), m. p. 225° (heated rapidly; when heated slowly it decomposes over a wide range) (Found: C, 72.5; H, 4.8; N, 6.8. $C_{22}H_{18}O_4N_2$ requires C, 72.35; H, 4.55; N, 7.0%). **1:7-Dihydroxynaphthalene**, micro-crystals, m. p. 174°, from ethanol (Found: C, 72.05; H, 4.8; N, 6.9%). **1:8-Dihydroxynaphthalene**, micro-needles (from glacial acetic acid), m. p. 229° (heated rapidly; decomposes gradually when heated slowly) (Found: C, 72.4; H, 4.3; N, 6.8%).

1:3-Di-1'-naphthyluretidione (**1:3-Di-1'-naphthyl-1:3-diazacyclobuta-2:4-dione**).—One drop of triethylamine was added to 1-naphthyl isocyanate (0.5 c.c.) and the mixture set aside in a stoppered tube. A few crystals rapidly appeared but three or four days elapsed before the whole mass solidified. Crystallisation from nitrobenzene and then from a large volume of boiling glacial acetic acid yielded colourless micro-needles, m. p. 295° (decomp. and sublimed) (Found: N, 8.3%. Calc. for $C_{22}H_{14}O_2N_2$: N, 8.3%). This corresponds to the compound obtained by Raiford and Freyermuth (*J. Org. Chem.*, 1943, **8**, 234) by the dimerisation of 1-naphthyl isocyanate in the presence of triethylphosphine.

Analyses are by Miss M. A. B. Davie. One of us (J. M. L.) thanks the Carnegie Trust for the Universities of Scotland for a scholarship.—CHEMISTRY DEPARTMENT, MARISCHAL COLLEGE, ABERDEEN. [Received, April 6th, 1950.]

Pregn-5-ene-3β:20β-diol. By W. KLYNE and E. MILLER.

WIELAND and MIESCHER (*Helv. Chim. Acta*, 1949, **32**, 1922) described the preparation of *pregn-5-ene-3β:20β-diol* by degradation of *3β-acetoxy-20-isonorchol-5-en-22-one* with perbenzoic acid. We had previously prepared this diol by reduction of *pregn-5-en-3β-ol-20-one* with lithium aluminium hydride. Ott and Murray (Amer. Chem. Soc. 113th Meeting, *Abstracts*, 1948, p. 17K) stated that they had reduced *pregnenolone* with this reagent, but gave no details. The reduction of other steroid ketones by lithium aluminium hydride has recently been described by Shoppee and Summers (*J.*, 1950, 687: previous references there).

We have shown that our *pregnenediol* and its diacetate are identical with the compounds described by Wieland and Miescher, to whom we are most grateful for samples. The constitution of our diol was checked by its conversion into *allopregnane-3β:20β-diol* on catalytic hydrogenation.

20β-Hydroxy-steroids have usually been made from C_{20} -ketones in the past by catalytic hydrogenation (see, e.g., Marker, Kamm, Jones, and Oakwood, *J. Amer. Chem. Soc.*, 1937, **59**, 614). Since this method is not suitable for the preparation of unsaturated *20β-hydroxy-compounds*, lithium aluminium hydride may be useful as a general reagent for making such compounds.

Experimental.—(All m. p.s are corrected. Micro-analyses are by Drs. Weiler and Strauss, Oxford. All rotations were determined at 20–25° for the sodium D line in chloroform, by using a 0.5-dm. micro-tube. Samples for the determination of rotations were dried for 2 hours at 80° in high vacuum. Light petroleum is the fraction, b. p. 40–60°.)

Pregn-5-ene-3β:20β-diol. *Pregn-5-en-3β-ol-20-one* (240 mg., 0.76 millimol.; m. p. 185–187°) was dissolved in dry benzene (10 c.c.) to which dry ether (30 c.c.) was added. This solution was added dropwise to a solution in ether (15 c.c.) of lithium aluminium hydride (202 mg., 5.32 millimol.), and the mixture was refluxed gently for 30 minutes. The solution was cooled and a mixture of ether (10 c.c.) and acetone (2 c.c.) was added to decompose the excess of lithium aluminium hydride. More ether (50 c.c.) was added and the mixture was shaken with 2N-sulphuric acid (30 c.c.) to dissolve aluminium hydroxide. The aqueous solution was extracted with ether (50 c.c.), and the combined ethereal extracts were washed successively with 2N-sulphuric acid (10 c.c.), water (30 c.c.), 2N-sodium carbonate solution (10 c.c.), and water (3 × 10 c.c.), dried (Na_2SO_4), and evaporated to dryness. The product (229 mg.) crystallised from acetone (7 c.c.) in rosettes of needles, m. p. 196–199° (124 mg.). Concentration of the mother-liquors afforded 40 mg. of similar material (total yield, 68%). This material on crystallisation from light petroleum-ethyl acetate gave silky needles, m. p. 201.5–203.5°, which contained one molecule of acetone of crystallisation (Found: C, 76.1; H, 10.7. Calc. for $C_{21}H_{34}O_2 \cdot C_3H_6O$: C, 76.5; H, 10.7. Calc. for $C_{21}H_{34}O_2$: C, 79.2; H, 10.8%). Crystallisation from methanol gave thick needles, m. p. 199–200°, which apparently contained half a molecule of methanol of crystallisation; mixed m. p. (with sample supplied by Wieland and Miescher) 200–202°: $[\alpha]_D^{20} - 65.3^\circ \pm 1.7^\circ$ (c, 0.77), $([\alpha]_D - 68.5^\circ$, calculated for substance without methanol of crystallisation); $[M]_D^{20} - 218^\circ$ (Found: C, 77.3; H, 10.7. Calc. for

$C_{21}H_{34}O_2 \cdot \frac{1}{2}CH_4O$: C, 77.2; H, 10.8%). Wieland and Miescher (*loc. cit.*) give m. p. 200.5—201.5°; $[\alpha]_D -64^\circ \pm 3^\circ$. The tetranitromethane test for unsaturation was positive; the Zimmermann keto-steroid reaction was negative.

Wieland and Miescher obtained the diol without solvent of crystallisation by sublimation at 150° in high vacuum. We were unable to repeat this; two samples sublimed at 160° and 5×10^{-4} mm. pressure gave analytical figures for carbon about 1% lower than those calculated for the unsaturated diol (Found: C, 77.9, 78.2; H, 10.6, 10.4. Calc. for $C_{21}H_{34}O_2$: C, 79.2; H, 10.8%).

Pregn-5-ene-3 β :20 β -diol diacetate. The pregnenediol was acetylated by heating it with acetic anhydride at 100° for 2 hours. The product was chromatographed on alumina (B. D. H.) and after three crystallisations from methanol containing 20% of water formed needles, m. p. 130—131°, $[\alpha]_D -36.6 \pm 1.0^\circ$ (*c*, 0.94); $[M]_D -147^\circ$ (Found, on a sample sublimed at $160^\circ/5 \times 10^{-4}$ mm.: C, 74.1; H, 9.5%. Calc. for $C_{23}H_{38}O_4$: C, 74.6, H, 9.5%). Mixed m. p. (with sample supplied by Wieland and Miescher) 127—128°. These authors (*loc. cit.*) give m. p. 125—126°; $[\alpha]_D -39^\circ \pm 2^\circ$.

Hydrogenation of pregn-5-ene-3 β :20 β -diol. The pregnenediol (36 mg.) was hydrogenated in the presence of Adams's platinum oxide catalyst (20 mg.) in glacial acetic acid (20 c.c.). The product, *allopregnane-3 β :20 β -diol*, crystallised from light petroleum-ethyl acetate in rosettes of leaflets, m. p. 194.5—195.5°; $[\alpha]_D +4.4^\circ \pm 1.0^\circ$ (*c*, 1.04); $[M]_D +14^\circ$ (Marker, Kamm, Jones, and Oakwood, *loc. cit.*, give m. p. 195—196°). Authentic *allopregnane-3 β :20 β -diol*, prepared by hydrolysis of the 3-acetate (Klyne and Barton, *J. Amer. Chem. Soc.*, 1949, **71**, 1500), had m. p. 194—195°, $[\alpha]_D +2.9^\circ \pm 0.9^\circ$ (*c*, 1.02): $[M]_D +9^\circ$. Mixed m. p. with the product of hydrogenation 195—196°.

The *allopregnenediol* obtained by hydrogenation was acetylated by heating it with acetic anhydride. The diacetate after crystallisation from light petroleum-ethyl acetate formed long needles, m. p. 141—142.5°; mixed m. p. 140—142° with authentic material (m. p. 140.5—142°, Klyne and Barton, *loc. cit.*).

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