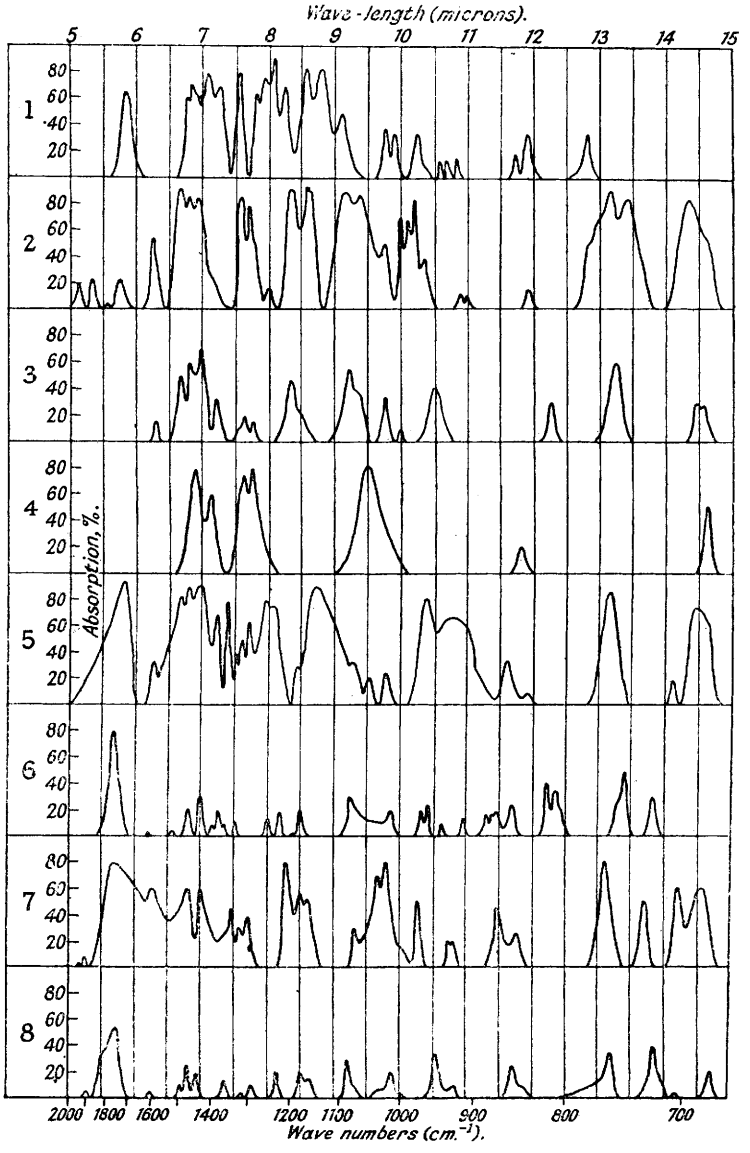
481. *The Infra-red Spectra of Three Sydnones and Certain N-Nitroso-compounds.*

By J. C. Earl, R. J. W. Le Fèvre, A. G. Pulford, and A. Walsh.

Present work.—Percentage absorptions of eight compounds listed below have been determined from 2 to 15 μ. by using the Perkin–Elmer model 12B recording infra-red spectrometer :

Compound and state.	Curve no. on Fig.
N-Nitrosotriacetonamine, as solidified layer	1
N-Nitrosodiphenylamine, as solidified layer	2
N-Nitrosomethylaniline, as liquid	3
N-Nitrosodimethylamine, as liquid	4
N-Nitrosophenylglycine, as suspension in Nujol	5
N-β-Naphthylsydnone, as suspension in Nujol	6
C-Bromo-*N*-phenylsydnone, as suspension in Nujol	7
N-Phenylsydnone, as suspension in Nujol	8



Comment.—In various *N*-nitrosoamides the –CO–N–N=O unit has been characterised by bands around 1490 and 1720 cm.$^{-1}$, ascribed respectively to >N–N=O and >C=O (cf. " The Chemistry of Penicillin," Princeton Univ. Press, 1949, pp. 152, 177).

Colthup (*J. Opt. Soc. Amer.*, 1950, **40**, 397) however assigns the absorption of the nitroso-group to the region 1310—1420 cm.$^{-1}$. From the Fig. it is seen that compounds 1—5 show absorption in common at *ca.* 1400 cm.$^{-1}$. Since Barredo and Goubeau (*Z. anorg. Chem.*, 1943, **251**, 2) and Wittek (*Anzeiger Akad. Wiss. Wien*, 1943, **3**, 5) have reported a Raman line at 1405 cm.$^{-1}$ for $Me_2N{\cdot}NO$ we relate this frequency to the *N*-nitroso-group in our substances. The non-occurrence of any such absorption with *N*-phenylsydnone (curve 8), and its weakness with the other two sydnones (curves 6 and 7), are of interest because hitherto the only evidence for the disappearance of the nitroso-group has been the failure of sydnones to respond to the qualitative Liebermann test (Earl and Mackney, *J.*, 1935, 899) and the general absence in the sydnones of chemical behaviour usually found in nitroso-compounds.

Curves 6—8 display strong absorptions at 1766, 1756, 1752 cm.$^{-1}$; these correspond approximately with the values listed by Hartwell, Richards, and Thompson (*J.*, 1948, 1436) for the " ester-carbonyl " group, and the maxima observed with the phenylglycine and triacetonamine derivatives (1722 and 1719 cm.$^{-1}$; curves 1 and 5) are nearer the values reported by the last authors for " carboxylic-carbonyl " group or simple aliphatic ketones. Nevertheless deductions regarding the states of these carbonyl groups might be dangerous since the sydnones are believed to contain a novel and resonating heterocyclic nucleus, and Hartwell, Richards, and Thompson (*loc. cit.*) have noted that where the >C=O is part of a ring its frequency is a complex function of ring-strain, of the natures of side-chain groups, of conjugation, and of other factors. Since the appropriate absorption in liquid *cyclo*pentanone occurs at 1744 cm.$^{-1}$, and in *cyclo*hexanone or acetone at 1714 or 1718 cm.$^{-1}$ respectively (Hartwell *et al.*, *loc. cit.*) ring-strain *alone* seems to cause an increase of some 30 cm.$^{-1}$ from the usual open-chain value. The effects of the other factors are unpredictable on the data at present available. Thus, while high >C=O frequencies (up to 1820 cm.$^{-1}$) have been recorded by Woodward (*J. Amer. Chem. Soc.*, 1950, **72**, 3327) for certain oxazolones and $\beta\gamma$-unsaturated five-ring lactones, contrarily a low frequency (1664 cm.$^{-1}$) is indicated by the Raman spectrum of antipyrin (Taboury and Boureau, *Bull. Soc. chim.*, 1945, [v], **12**, 594)—a molecule in which carbonyl polarisation of the type $>C\overset{\curvearrowright}{=}O$ is evident from other directions (cf. *J.*, 1949, 2812). In the light of previous discussions (cf. particularly, *J.*, 1948, 2269; 1949, 103, 307, 746; *J. Chim. physique*, 1949, **46**, 244) on the sydnones, coupled with the considerations set out by Walsh (*Trans. Faraday Soc.*, 1947, **43**, 158; *Ann. Reports*, 1947, **44**, 45) and Schneider and Halverstadt (*J. Amer. Chem. Soc.*, 1948, **70**, 2626), we expected at the outset that their ketonic frequencies would probably resemble that in antipyrin. At the same time, the absorptions observed (1750—1770 cm.$^{-1}$) are sufficiently low (cf. Thompson and Linnett, *J.*, 1937, 1291; Drayton and Thompson, *J.*, 1948, 1416) to suggest insignificant contributions of the keten-like structure already dismissed by Baker, Ollis, and Poole (*J.*, 1949, 307) on stereochemical grounds.

Incidentally the appearance of a regular ketonic band in *N*-nitrosophenylglycine, considered against the results of Slovochotova, Sirkin, and Volkenstein (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, **35**, 146) for betaine, further confirms the rejection of " zwitterion " formulations for the precursors of the sydnones (cf. *J.*, 1948, 2269; 1949, 5103).

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482. *Trichloromethylamine (Aminochloroform).*

By K. R. Simon Ascher.

There is no reference in the literature to a successful synthesis of trichloromethylamine (aminochloroform), though several unsuccessful attempts to prepare it have been recorded : (1) Spiegel and Spiegel (*Ber.*, 1907, **40**, 1733) attempted to prepare it by a Curtius reduction, but as they failed to obtain trichloroacetazide they concluded that the radicals $\cdot N_3$ and $\cdot CCl_3$ are incompatible. (2) Reduction of chloropicrin also failed : among the reducing agents used were stannous chloride and hydrochloric acid (Raschig, *Ber.*, 1885, **18**, 3326), iron and acetic acid (Geisse, *Annalen*, 1859, **109**, 282), iron filings and dilute hydrochloric acid (Frankland *et al.*, *J.*, 1919, **115**, 161), and potassium pyrosulphite (Geisse, *loc. cit.*).

Two workers may have encountered trichloromethylamine during their work, but they do not state the fact explicitly. Henderson and Macbeth (*J.*, 1922, **121**, 892) found, but without recording experimental details, that : " hydrazine removes one of the chlorine atoms from chloropicrin very slowly in the cold. Potassium ferrocyanide is without action. *Titanous chloride reduces the nitro-group, but leaves the halogen unattacked.*" Piutti (*Gazzetta*, 1921, **51**, I, 148) stated that solutions of chloropicrin in methyl alcohol or ethyl alcohol separate after one day into two layers with precipitation of ammonium chloride, and assumed that the alcohols reduce the nitro- to an amino-group, which is then split off as ammonia.

There appears to be no reference to a synthesis of $NH_2 \cdot CHX_2$ and $NH_2 \cdot CH_2X$ (X = halogen), but Hinkel and Watkins (*J.*, 1944, 647) inferred from the final products of the reaction between hydrogen chloride and hydrogen cyanide that dichloromethylamine appears as an intermediate product in the *reaction*.

It was found that trichloromethylamine could be obtained by a slightly modified Hofmann degradation.

Experimental.—To 16·5 g. of trichloroacetamide are added, with cooling and stirring, 16 g. (5·2 ml.) of bromine, followed by cold aqueous potassium hydroxide (40 g. in 280 ml.) until the colour of the solution turns from a red-brown to a bright yellow. Then the solution is poured into aqueous potassium hydroxide (16 g. in 30 ml.) previously heated to 70—75°. The solution becomes strongly opalescent and is kept at 70—75° until the yellow colour disappears (*ca.* 1 minute). Then, *immediately*, the solution is cooled in ice, after which it is extracted many times with small quantities of ether (until it clears). The ethereal extract is dried (Na_2SO_4), and the ether allowed to evaporate in a large porcelain dish at room temperature. The residue, when further dried in a desiccator over phosphoric oxide, affords a viscous oil (yield, 10%), with a smell resembling that of carbon tetrachloride. *Trichloromethylamine* (Found : N, 10·3; Cl, 79·0. CH_2NCl_3 requires N, 10·4; Cl, 79·2%) has b. p. 109° and is not inflammable. It is strongly acidic, owing to the inductive influence of the chlorine atoms on the hydrogen (cf. nitramine), and reacts with aqueous silver nitrate to give the compound $NHAg \cdot CCl_3$, which is insoluble in concentrated ammonium hydroxide. Trichloromethylamine seems to possess some ovicidal properties against eggs of *Pediculus humanus corporis* (body louse).

Use of hypochlorite instead of hypobromite leads to a violent reaction, with evolution of ammonia, and no trichloromethylamine is produced.

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483. *The Reaction of Aromatic Hydrocarbons with Lithium Aluminium Hydride, and a New Technique for the Use of the Reagent.*

By Isaac Goodman.

It is known (Goodman, *J.*, 1951, 846) that anthracene, unlike phenanthrene, is reduced to the dihydro-compound by reaction with lithium aluminium hydride at about 220°, and it was of interest to examine whether the reduction of other aromatic hydrocarbons could be effected under milder conditions.

When lithium aluminium hydride is warmed with " Carbitol," a slow evolution of hydrogen commences at about 70° and at 90—95° a violent reaction ensues, which, if suitably controlled, yields a clear colourless solution possessing powerful reducing properties; thus it reduces acenaphthylene to acenaphthene. The reaction with " Carbitol " presumably yields an alkoxide form of the elements of the reagent, either as a complex compound or as a mixture of metal alkoxides (cf. Solms, *Chimia*, 1951, **5**, 25; Krajkeman, *Mfg. Chem.*, 1951, **22**, 147); it is noteworthy, however, that although the hydride dissolves readily in *n*-butanol, the resulting solution does not reduce acenaphthylene.

Advantages of the new reagent are : (*a*) it presents a stable reducing agent at temperatures up to the boiling point of " Carbitol " (approximately 200°), and (*b*) the vigorous reaction generally obtained in the hydrolysis of the excess of lithium aluminium hydride is avoided.

Dilution of the " Carbitol " reagent with water precipitates the metal hydroxides without evolution of heat; reaction with hydrocarbons followed by direct hydrolysis with dilute acid gives the reaction-product as a precipitate free from other organic matter.

Unless great care is exercised in the preparation of the reagent, the reaction above 90° becomes uncontrollably violent, particles of the hydride becoming incandescent and causing considerable carbonisation. To avoid this the reaction must be conducted in nitrogen, and the hydride used as a very fine powder with suitable agitation, and cooling when necessary. The reagent should be prepared in a considerable excess of " Carbitol."

Addition of acenaphthylene to the " Carbitol " reagent resulted in the immediate, almost quantitative reduction to acenaphthene, whereas acenaphthylene was recovered unchanged (in 95% yield) after being heated under reflux with the hydride in ether for 5 hours. Anthracene was recovered unchanged (in 97% yield) after being heated for 3 hours with the " Carbitol "–lithium aluminium hydride reagent at the boiling point of the solvent (cf. the " dry " reaction which gave a 56% yield of dihydroanthracene at substantially the same temperature). Pyrene, which is not reduced in ether solution by the hydride, was similarly recovered unchanged in the " Carbitol " method. Naphthacene, pentacene, and perylene were equally not reduced by the " Carbitol "–hydride reagent or by the solid reagent in boiling naphthalene solution. 9 : 9′-Difluorenylidene was reduced in ether solution to 9 : 9′-difluorenyl, the same product also being obtained when difluorenylidene was refluxed in ethanol with Raney nickel (cf. Mozingo, Spencer, and Folkins, *J. Amer. Chem. Soc.*, 1944, **66**, 1859).

The formation of the dihydro-compound when anthracene was heated with lithium aluminium hydride above the decomposition temperature of the latter remains the sole example of the reduction of an aromatic ring by this reagent, and it is probable that such rings are indeed immune to lithium aluminium hydride, and that the reduction of anthracene is a heterogeneous reaction brought about by liberated hydrogen on a catalytic surface made available during the decomposition of the reagent.

Reduction of Acenaphthylene to Acenaphthene.—(i) *Pre-formation of the reagent.* " Carbitol " (50 c.c.) and lithium aluminium hydride (1 g.) were warmed, the precautions already described being observed. At 95° a violent reaction began, with spontaneous rise of temperature to 120°. Acenaphthylene (1 g.) in " Carbitol " (10 c.c.) was added to the cooled solution, the yellow colour being immediately discharged. The mixture was warmed for 15 minutes at 100° and then hydrolysed. The product (0·85 g.) formed very pale yellow crystals, m. p. 88—93°, from ethanol.

(ii) *Without pre-formation of the reagent.* Acenaphthylene (1 g.) and finely powdered lithium aluminium hydride (1 g.) were warmed at 120° for 3 hours in " Carbitol " (20 c.c.); during this period a quantity of dark grey inorganic solid agglomerated at the bottom of the reaction mixture. Decomposition with dilute hydrochloric acid did not cause any temperature increase. The greyish product (97%) was crystallised from ethanol, giving acenaphthene (0·8 g.), m. p. 89—93°.

The thermal equilibrium diagram for the system acenaphthene–acenaphthylene (Kynaston and Idris Jones, *J. Soc. Chem. Ind.*, 1949, **68**, 228) permitted both products to be determined as acenaphthene of 96% purity (confirmed by the melting-point depression obtained when very small quantities of acenaphthylene were added).

[ADDED, May 6th, 1951.] *Reduction of 9 : 9′-Difluorenylidene to 9 : 9′-Difluorenyl.*—(i) *With lithium aluminium hydride.* The hydrocarbon (0·05 g.) and lithium aluminium hydride (0·5 g.) were refluxed in ether (30 c.c.) for 5½ hours. The solution was decomposed with dilute sulphuric acid, and the product isolated from the ethereal layer as a yellow solid, m. p. 224—232°. Crystallisation from *n*-butanol gave needles of 9 : 9′-difluorenyl (0·039 g., 77·5%), m. p. 241—242° (cf. de la Harpe and van Dorp, *Ber.*, 1875, **8**, 1049; Wanscheid, *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 252, 280, 282).

(ii) *With Raney nickel.* Raney nickel (from 40 g. of the alloy) was washed with water until the wash-liquor pH fell to 9·5. The water was decanted, and absolute ethanol (100 c.c.) and 9 : 9′-difluorenylidene

(1 g.) added. After 4 hours' refluxing the red colour of the hydrocarbon had disappeared. Evaporation of the solution gave 9 : 9′-difluorenyl (0·2 g.), m. p. 237—240° raised by crystallisation from butanol (charcoal) to 242°.

The author is indebted to Mr. W. F. Maddams of the Physics Department, Manchester Oil Refinery, Ltd., who kindly made available samples of naphthacene, pentacene, and perylene.

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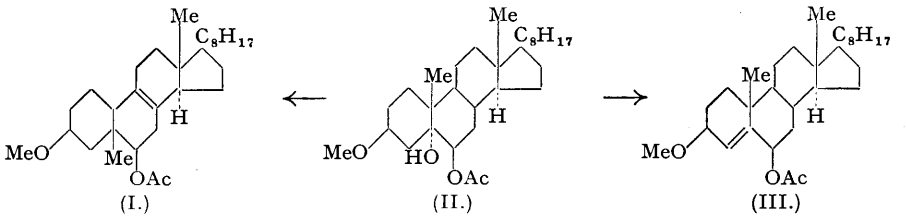
484. *The Dehydration of 6β-Acetoxy-3β-methoxycholestan-5α-ol.*

By M. DAVIS and V. PETROW.

THE constitution 6β-acetoxy-3β-methoxycholest-4-ene (III) previously assigned (Petrow, *J.*, 1937, 1077) to the product obtained by dehydrating 6β-acetoxy-3β-methoxycholestan-5α-ol (II) with sulphuric acid–acetic anhydride, requires revision in the light of subsequent work.



We find that the properties of the foregoing dehydration product are more consistent with its formulation as a 6β-acetoxy-3β-methoxy-5-methyl-19-norcholest-8(9)-ene (I) than as (III). Thus the compound is unsaturated towards tetranitromethane. It fails to give a colour with the trichloroacetic acid reagent, but gives a typical green colour in the Tortelli–Jaffé reaction (cf. Petrow, Rosenheim, and Starling, *J.*, 1938, 677). It shows a high positive rotation, retained in the 6-hydroxy-compound, but changed in sign in the 6-keto-derivative (cf. Davis and Petrow, *J.*, 1949, 2973). The conclusion that the compound belongs to the " Westphalen " series thus appears to be inescapable.

Additional evidence supporting this view is that dehydration of (II) with thionyl chloride–pyridine (cf. Petrow, Rosenheim, and Starling, *loc. cit.*) gives a new compound, isomeric with (I), which gives a blue colour with trichloroacetic acid and is thus the authentic 6β-acetoxy-3β-methoxycholest-4-ene (III).

Experimental.—M. p.s are corrected. Optical rotations were measured in chloroform solution. Microanalyses are by Drs. Weiler and Strauss, Oxford.

6β-Acetoxy-3β-methoxycholest-4-ene (III). Redistilled thionyl chloride (0·2 ml.) was added to a solution of 6β-acetoxy-3β-methoxycholestan-5α-ol (1 g.) (Petrow, *loc. cit.*) in dry pyridine (5 ml.). After 1·5 hours at room temperature the solution was poured into water. *6β-Acetoxy-3β-methoxycholest-4-ene* (0·9 g.) separated and crystallised from methanol as needles, m. p. 93—94° (Found : C, 78·5; H, 10·6. $C_{30}H_{50}O_3$ requires C, 78·5; H, 11·0%). *3β-Methoxycholest-4-en-6β-ol*, obtained by hydrolysis of the acetate with ethanolic potassium hydroxide, crystallised from alcohol as needles, m. p. 171—173° (Found : C, 79·4; H, 11·3. $C_{28}H_{48}O_2,\frac{1}{2}H_2O$ requires C, 78·9; H, 11·6%).

6-Acetoxy-3-methoxy-5-methyl-19-norcholest-8(9)-ene (I) was prepared in 48—52% yield by dehydration of 6β-acetoxy-3β-methoxycholestan-5α-ol with potassium hydrogen sulphate–acetic anhydride. (cf. Petrow, *J.*, 1939, 998). Hydrolysis with 5% ethanolic potassium hydroxide gave *3-methoxy-5-methyl-19-norcholest-8(9)-en-6-ol*, which separated from aqueous alcohol as needles, m. p. 108°, $[\alpha]_D^{14}$ +119·4° ± 0·6° (*c*, 1·575) (Found : C, 80·6; H, 11·8. $C_{28}H_{48}O_2$ requires C, 80·8; H, 11·6%). The *6-benzoyl* derivative, prepared by boiling the hydroxy-compound with benzoyl chloride in pyridine for 1 hour, formed fine needles, m. p. 91—92°, from acetone–methanol (Found : C, 80·4; H, 10·0. $C_{35}H_{52}O_3$ requires C, 80·7; H, 10·1%).

3-Methoxy-5-methyl-19-norcholest-8(9)-en-6-one. 3-Methoxy-5-methyl-19-norcholest-8(9)-en-6-ol (1 g.) in benzene (10 ml.) was shaken for 5 hours at room temperature with chromium trioxide (0·33 g.) in 70% acetic acid (15 ml.). The neutral fraction of the product, when crystallised from acetone–methanol, yielded *3-methoxy-5-methyl-19-norcholest-8(9)-en-6-one* (50—55%) in feathery needles, m. p. 65—66°, $[\alpha]_D^{14}$ −4·6° ± 0·8° (*c*, 1·310) (Found: C, 81·3; H, 10·9. $C_{28}H_{46}O_2$ requires C, 81·1; H, 11·2%). The 2 : 4-*dinitrophenylhydrazone*, m. p. 125—127°, crystallised from chloroform–methanol (Found: N, 9·1. $C_{34}H_{50}O_5N_4$ requires N, 9·4%).

3-Methoxy-5-methyl-19-norcholest-8(9)-en-6-yl sulphite. A solution of 3-methoxy-5-methyl-19-norcholest-8(9)-en-6-ol (0·1 g.) in pyridine was treated with thionyl chloride (0·1 ml.) and kept at room temperature for 24 hours. The *sulphite* obtained by pouring the mixture into water and extraction with ether separated from acetone as needles, m. p. 191° (Found: C, 76·6; H, 10·8; S, 3·45. $C_{56}H_{94}O_5S$ requires C, 76·5; H, 10·8; S, 3·6%).

One of us (M. D.) thanks the Department of Scientific and Industrial Research for a maintenance allowance.

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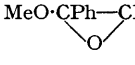
485. *The Formation of Osazones. Part III.**

By G. J. BLOINK and K. H. PAUSACKER.

TEMNIKOVA and KROPACHEVA (*J. Gen. Chem., U.S.S.R.*, 1949, **19**, 1917; cf. *Chem. Abs.*, 1950, **44**, 1929) claim that 1 : 2-epoxy-1-methoxy-1-phenylpropane (I) reacts with phenylhydrazine, in ethyl alcohol containing acetic acid, to form (II), m. p. 126°.



(I.)

NHPh·N:CPh·CHMe·NH·NHPh (II.)

NHPh·N:CPh·CMe:N·NHPh (III.)

This result is unusual for it would be expected that (II) would be converted into 1-phenyl-1 : 2-di(phenylhydrazono)propane (III), m. p. 105°, which has previously been prepared by Müller and von Pechmann (*Ber.*, 1889, **22**, 2127). Compounds similar to (II) have previously been postulated only as labile intermediates in osazone formation (cf. Weygand and Reckhaus, *Ber.*, 1949, **82**, 442), it being assumed that they are readily oxidised by phenylhydrazine.

Repetition of Temnikova and Kropacheva's work gave a compound, m. p. 128°, which was identical (mixed m. p.) with 1-acetyl-2-phenylhydrazine (Found: C, 64·0; H, 6·4; N, 18·7. Calc. for $C_8H_{10}ON_2$: C, 64·0; H, 6·7; N, 18·7%). Fischer (*Annalen*, 1878, **190**, 270) gives m. p. 128·5°; Andeslini (*Ber.*, 1891, **24**, 1993, footnote) has shown that phenylhydrazine is readily acetylated, even in aqueous acetic acid, so that the compound assigned structure (II) is therefore 1-acetyl-2-phenylhydrazine.

When *p*-chlorophenylhydrazine reacted with (I) under the same conditions, colourless crystals of 1-acetyl-2-*p*-chlorophenylhydrazine, m. p. 157°, were isolated (Found: C, 51·6; H, 4·9; N, 15·3. Calc. for $C_8H_9ON_2Cl$: C, 52·0; H, 4·9; N, 15·2%). Von Pechmann and Vanino (*Ber.*, 1894, **27**, 224) give m. p. 154°. When 1-phenylpropane-1 : 2-dione was condensed with *p*-chlorophenylhydrazine, yellow needles of 1 : 2-*di*-(p-*chlorophenylhydrazono*)-1-*phenylpropane* were formed; after crystallisation from ethanol they had m. p. 157° (mixed m. p. with 1-acetyl-2-*p*-chlorophenylhydrazine 139°) (Found: C, 63·1; H, 4·9; N, 13·8; Cl, 18·3. $C_{21}H_{20}N_4Cl_2$ requires C, 63·1; H, 5·0; N, 14·0; Cl, 17·8%).

It is thus apparent that hydrazino-hydrazones, such as (II), are not formed when (I) reacts with phenylhydrazines.

Microanalyses are by Dr. W. Zimmermann.

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* Part II, *J.*, 1951, 622.

486. *The Bromination of o-Acylaminotoluenes. A Correction.*

By D. G. I. Felton.

Leulier and Arnoux (*Bull. Soc. chim.*, 1930, **47**, 730; see also Leulier, *ibid.*, 1924, **35**, 1325; 1926, **39**, 29; Leulier and Pinet, *ibid.*, 1927, (4), **41**, 1362), in the course of the formers' study of halogenation by means of hydrogen halide–aqueous hydrogen peroxide, reported that treatment of *o*-acetamidotoluene with hydrobromic acid and perhydrol yielded 2-acetamido-5-bromotoluene as needles, m. p. 156—157°, whereas the same reagents with *o*-benzamidotoluene afforded 2-benzamido-6-bromotoluene, m. p. 175—176°. This surprising implication of a variation in the directive influence of an acylamino-group depending upon the acyl group, on which Leulier and Arnoux did not even comment, warranted further examination. The French workers did not prove the orientation of their products chemically, but relied on a comparison of the melting points with those quoted in the literature :

Toluene.	M. p.	Reference.
2-Acetamido-5-bromo-	156—157°	Bogert and Hand, *J. Amer. Chem. Soc.*, 1905, **27**, 1479.
2-Acetamido-6-bromo-	154—155	Cohen and Miller, *J.*, 1904, **85**, 1627.
	158	Noelting, *Ber.*, 1904, **37**, 1022.
2-Benzamido-5-bromo-	115	Ressy and Ortodocsu, *Bull. Soc. chim.*, 1923, (4), **33**, 639.
2-Benzamido-6-bromo-	176—177	Cohen and Miller, *loc. cit.*

The orientation of all of these compounds had been rigorously established except that of 2-benzamido-5-bromotoluene, which Ressy and Ortodocsu had prepared by bromination of *o*-benzamidotoluene in acetic acid solution by bromine.

On investigation, the observations of Leulier and Arnoux were confirmed, and the bromo-derivatives of *o*-acetamido- and *o*-benzamido-toluenes were found to melt at 157—158° and 174—175°, respectively. However, hydrolysis of 2-benzamido-*x*-bromotoluene with 70% sulphuric acid, followed by acetylation of the isolated amine, yielded 2-acetamido-*x*-bromotoluene, m. p. 159—160°, undepressed on admixture with the bromo-derivative obtained from *o*-acetamidotoluene by the method described by Leulier and Arnoux. Thus these authors' suggestion of a variation in the directive influence of an acylamino-group was not sustained.

However, there still remained the orientation of the bromine atom, especially in view of the close correspondence in the melting points of the 5- and the 6-bromo-derivative of *o*-acetamidotoluene. It seemed unlikely that bromination could occur in any position other than *p*- to the acylamino-group. Accordingly, the bromination of *o*-benzamidotoluene was repeated following the directions given by Ressy and Ortodocsu (*loc. cit.*), whereupon a bromo-derivative, m. p. 174—175°, was isolated, the m. p. of which was undepressed by Leulier and Arnoux's bromo-compound. Apparently the m. p. 115° quoted in the literature is a typographical error. The possible confusion of m. p.s was now complete. Both the 5- and the 6-bromo-derivative of *o*-acetamidotoluene melt at the same temperature and the same now appears true of the derivatives of *o*-benzamidotoluene. For a rigorous orientation, the 2-acetamido-*x*-bromotoluene was oxidised by potassium permanganate in aqueous magnesium sulphate at 80—85° to the corresponding benzoic acid, m. p. 219—221° [cf. 2-acetamido-5-bromobenzoic acid, m. p. 223—224° (Bogert and Hand, *loc. cit.*); 2-acetamido-6-bromobenzoic acid, m. p. 224° (Friedländer, Bruckner, and Deutsch, *Annalen*, 1912, **388**, 30)], and this was deacetylated by refluxing it with 50% sulphuric acid yielding *x*-bromoanthranilic acid as needles, m. p. 213—214° (decomp.). This was shown to be identical (mixed m. p.) with 5-bromoanthranilic acid, prepared by Wheeler (*J. Amer. Chem. Soc.*, 1909, **31**, 565) by direct bromination of anthranilic acid dissolved in acetic acid, and orientated by him by deamination *via* the diazonium salt to *m*-bromobenzoic acid.

Consequently, bromination of *o*-acylaminotoluenes with hydrobromic acid and perhydrol, following the directions of Leulier and Arnoux proceeds normally to yield 2-acylamino-5-bromotoluenes.

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487. *A New Synthesis of* 4 : 6-*Dihydroxypyrimidines.*

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Comparatively few pyrimidines unsubstituted in position 2 have been described, and before 1943 these had been synthesised by elimination of a suitable substituent from that position. However, Kenner, Lythgoe, Todd, and Topham (*J.*, 1943, 388) reported that 4 : 6-dihydroxypyrimidine was synthesised from formamidine and diethyl malonate, and later (*J.*, 1943, 574) that the corresponding diamino-compound was formed from ethyl formate and malondiamidine. It is now shown that by substituting malondiamide for malondiamidine in the latter synthesis, the expected 4 : 6-dihydroxypyrimidine is obtained in satisfactory yield. This is the more convenient synthesis of this compound.

Reaction of the diamide and the ester was carried out in the presence of sodium ethoxide, and the product on treatment with phosphoryl chloride gave 4 : 6-dichloropyrimidine, undepressed in melting point on admixture with an authentic specimen (*ibid.*; *J.*, 1943, 575).

The reaction appears to be general, for phenyl- and ethyl-malondiamide which were treated in like fashion gave the corresponding 5-phenyl- and 5-ethyl-4 : 6-dihydroxypyrimidines.

Experimental.—4 : 6-*Dihydroxypyrimidine.* Malondiamide (10·2 g.) was added to alcoholic sodium ethoxide (4·6 g. of sodium in 150 c.c. of alcohol), followed by ethyl formate (11·0 g.), and the mixture heated under reflux for 2 hours. Next morning the solid was collected, washed with alcohol, and dissolved in water (50 c.c.). The solution was acidified with 5N-hydrochloric acid, and the solid (4·5 g.) collected. Crystallisation from water gave the product as microprisms, which on being dried became yellow, m. p. >300° (Found : C, 42·75; H, 4·0; N, 25·05. Calc. for $C_4H_4O_2N_2$: C, 42·8; H, 3·6; N, 25·0%).

4 : 6-*Dichloropyrimidine.* 4 : 6-Dihydroxypyrimidine (0·5 g.) was heated under reflux with phosphoryl chloride (7 c.c.) and dimethylaniline (0·26 c.c.) for 3 hours. After cooling, the reaction mixture was poured on ice and extracted with ether. The extract was washed with sodium carbonate solution, dried, and evaporated. The product (0·5 g.) set to yellow needles, m. p. 63·5—64° undepressed by authentic 4 : 6-dichloropyrimidine (*loc. cit.*, p. 575).

4 : 6-*Dihydroxy-5-phenylpyrimidine.* Phenylmalondiamide (8·9 g.) (Dox and Yoder, *J. Amer. Chem. Soc.*, 1922, **44**, 1566) was added to alcoholic sodium ethoxide (2·3 g. of sodium in 75 c.c. of alcohol), followed by ethyl formate (8·05 c.c.), and the mixture was refluxed for 2 hours. After cooling, the solid was digested with warm water (50 c.c.) and filtered from unreacted phenylmalondiamide [2·35 g., m. p. 221—222° (decomp.)], and the filtrate acidified with hydrochloric acid. The pyrimidine (3·55 g.) was collected and washed with a small quantity of water. Crystallisation from water gave microneedles of 4 : 6-*dihydroxy*-5-*phenylpyrimidine*, m. p. >300° (Found : C, 63·85; H, 4·0; N, 14·85. $C_{10}H_8O_2N_2$ requires C, 63·8; H, 4·25; N, 14·9%).

5-*Ethyl*-4 : 6-*dihydroxypyrimidine.* Ethylmalondiamide (7·4 g.), alcoholic sodium ethoxide (2·6 g. of sodium in 90 c.c. of alcohol), and ethyl formate (6·3 g.) were refluxed for 2 hours. Next morning the solid was collected, and combined with the residue left after evaporation of the solvent from the filtrate. The combined solids were dissolved in warm water (80 c.c.) and extracted with ether, and the aqueous layer was acidified (hydrochloric acid). The solid (3·3 g.) was collected and washed with water. Crystallisation from water gave prismatic needles of 5-*ethyl*-4 : 6-*dihydroxypyrimidine*, m. p. >300° (Found : C, 51·4; H, 5·85; N, 20·0. $C_6H_8O_2N_2$ requires C, 51·4; H, 5·7; N, 20·0%).

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