NOTES.

The Nitration of 4-*Hydroxyquinoline.* By A. ADAMS and D. H. HEY.

IN a recent communication Gouley, Moersch, and Mosher (*J. Amer. Chem. Soc.*, 1947, **69**, 303) have reported the nitration of 4-hydroxyquinoline at 0—5°. They obtained in 91% yield a mixture of nitro-4-hydroxyquinolines which on treatment with phosphorus oxychloride gave a mixture of 4-chloronitroquinolines, from which a compound regarded as 4-chloro-3-nitroquinoline, m. p. 145°, was isolated in approximately 50% yield. To some extent the experimental evidence points to the formation of the 6-nitro- rather than the 3-nitro-compound. The m. p. of the crude nitration product (290—301°) is nearer the value of 325° (corr.) for the m. p. of 6-nitro-4-hydroxyquinoline reported by Bachman and Cooper (*J. Org. Chem.*, 1944, **9**, 303), and that of 290—295° (decomp.) for the crude compound by Baker, Lappin, Albisetti, and Riegel (*J. Amer. Chem. Soc.*, 1946, **68**, 1267), than that of >325° for the m. p. of 3-nitro-4-hydroxyquinoline, reported by Bachman, Welton, Jenkins, and Christian (*J. Amer. Chem. Soc.*, 1947, **69**, 368). Further, Gouley, Moersch, and Mosher's 4-chloronitroquinoline, m. p. 145°, which depressed the melting point of 4-chloro-5-nitroquinoline (m. p. 150°), melts at a temperature nearer that of the m. p. of 4-chloro-6-nitroquinoline, reported by Baker, Lappin, Albisetti, and Riegel (*loc. cit.*) as 141—141·5° and by Bachman and Cooper (*loc. cit.*) as 142·5°, than that of 4-chloro-3-nitroquinoline, first reported by Bachman, Welton, Jenkins, and Christian (*loc. cit.*) as 121—122°. The constitution put forward by Gouley, Moersch, and Mosher is based on the fact that, after reducing their 4-chloronitroquinoline first with iron powder and then with Raney nickel, they obtained an aminoquinoline, m. p. 94°, regarded as 3-aminoquinoline. 3-Aminoquinoline is reported by Mills and Watson (*J.*, 1910, 746) to melt at 94°, whereas 6-aminoquinoline is reported by La Coste (*Ber.*, 1883, **16**, 672) to melt at 114° (not 107° as stated by Gouley, Moersch, and Mosher).

The nitration of 4-hydroxyquinoline has now been repeated, using the conditions described by Gouley, Moersch, and Mosher, and the nitration product, after crystallisation from glacial acetic acid, showed a depression in m. p. when mixed with an authentic specimen of 3-nitro-4-hydroxyquinoline, prepared as described by Bachman, Welton, Jenkins, and Christian (*loc. cit.*). The nitro-4-hydroxyquinoline was treated with phosphorus oxychloride to give a 4-chloronitroquinoline, m. p. 142·5—143°, which, when heated with *p*-chloroaniline, gave 6-nitro-4-*p*-chloroanilinoquinoline, identified by a mixed m. p. with an authentic specimen. The main product of the nitration of 4-hydroxyquinoline under the experimental conditions used is thus shown to be 6-nitro-4-hydroxyquinoline.*

6-*Nitro*-4-*hydroxyquinoline* (cf. Gouley, Moersch, and Mosher, *loc. cit.*).—A cooled mixture of concentrated sulphuric acid (10 c.c.) and fuming nitric acid (*d* 1·5; 10 c.c.) was added, with stirring, over a period of 45 minutes, to a solution of 4-hydroxyquinoline (10·0 g.) in concentrated sulphuric acid (45 c.c.). The mixture was kept at 0—5° during the addition, and for 1½ hours afterwards. The product was poured on crushed ice (500 g.), and basified with ammonia. The precipitate was collected, washed with water, and dried. The crude 6-nitro-4-hydroxyquinoline was obtained as a yellow crystalline powder (9·9 g.), m. p. 275—290°. Recrystallisation gave a yellow crystalline powder, m. p. 308—313° (from ethanol), and greenish-white needles, m. p. 310—315° (from glacial acetic acid). The products showed no depression in m. p. when mixed together, but each gave a depression when mixed with an authentic specimen of 3-nitro-4-hydroxyquinoline. Evaporation of the ammoniacal filtrate gave 4-hydroxyquinoline (0·8 g.).

6-*Nitro*-4-p-*chloroanilinoquinoline*.—6-Nitro-4-hydroxyquinoline (7·2 g.) was refluxed with phosphorus oxychloride (30 c.c.) for 90 minutes, and the mixture cooled and poured on ice. The solution was made just alkaline with ammonia, and the precipitated 4-chloro-6-nitroquinoline collected, washed with water, dried, and recrystallised from methanol (6·4 g.; m. p. 142·5—143°). A mixture of 4-chloro-6-nitroquinoline (2·6 g.) and *p*-chloroaniline (1·5 g.) was heated at 210°; the temperature quickly rose to 300°, and was kept there for 10 minutes. The product was then cooled, and dissolved in glacial acetic acid. The solution was diluted with water, filtered from a black insoluble impurity, and neutralised with aqueous potassium hydroxide. The precipitated 6-nitro-4-*p*-chloroanilinoquinoline was collected, washed with water, and dried. It was obtained as a yellow-brown crystalline powder (2·2 g.), m. p. 214—223°. Repeated recrystallisation from toluene raised the m. p. to 235—237°, which was not depressed on admixture with an authentic specimen prepared as described by Bennett, Crofts, and Hey (this vol., p. 227).

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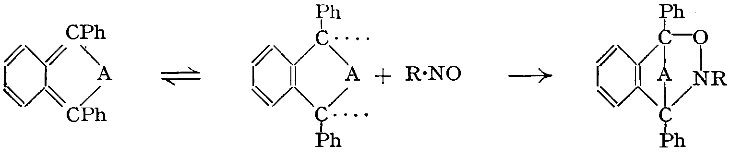
* Since this communication was submitted for publication, Schofield and Swain (*Nature*, 1948, **161**, 690) have also drawn attention to the fact that the main nitration product of 4-hydroxyquinoline is the 6-nitro-derivative.

The authors wish to express their thanks to Miss W. J. Hawkes for an authentic specimen of 3-nitro-4-hydroxyquinoline, and to Dr. P. C. Crofts for an authentic specimen of 6-nitro-4-*p*-chloroanilinoquinoline.—KING'S COLLEGE (UNIVERSITY OF LONDON), STRAND, LONDON, W.C.2. [*Received, March 30th*, 1948.]

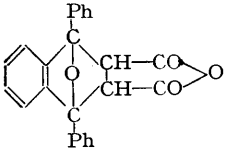
Action of Aromatic Nitroso-compounds on 1 : 3-*Diphenyl*iso*benzofuran*. By AHMED MUSTAFA.

THE action of aromatic nitroso-compounds on 1 : 3-diphenyl*iso*benzofuran (I) has not hitherto been reported. With nitrosobenzene and *p*-nitrosodimethylaniline it gives the addition *compounds* (III and IV), respectively. This reaction may be explained by assuming that (I) dissociates and the free radical (I*a*), thus produced (cf. Adams and Gold, *J. Amer. Chem. Soc.*, 1940, **62**, 2038), reacts with the nitroso-group (compare the interaction of nitrosobenzene and the triphenylmethyl radical; Goldschmidt and Christman, *Annalen*, 1925, **442**, 246) :

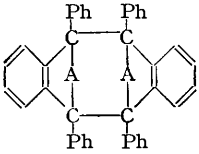


(I, A = O; II, A = S.) (I*a*; A = O.) (III, A = O, R = Ph; **IV**, A = O, R = p-C_6H_4·NMe_2; V, A = S, R = Ph.)

The fact that the addition products (III and IV) are almost colourless and decompose when heated at 270°, giving (I) [compare the thermal decomposition of the addition compound (VI), obtained by the action of maleic anhydride on (I), into its generators (Barnett, *J.*, 1935, 1326)], favours the given structure. When the thermal decomposition of (III) was carried out at 270° in a sealed tube and the melt chilled in ice-water as soon as possible, the compound (VII*a*) was obtained (cf. Schönberg and Mustafa, *Nature*, 1947, **160**, 401; Schönberg *et al.*, *J.*, 1948, 2126).



(VI.)



(VII*a*, A = O; VII*b*, A = S.)

On the other hand, the sulphur analogue of (I), 1 : 3-diphenyl*iso*benzothiophen (II), is stable to the action of maleic anhydride in boiling xylene (Dufraisse and Daniel, *Bull. Soc. chim.*, 1937, **4**, 2063); it is also stable to the action of nitrosobenzene and does not undergo dimerisation when its benzene solution is exposed to sunlight [compare the dimerisation of (I) in sunlight (Guyot and Catel, *ibid.*, 1906, **35**, 1127) or by the action of heat (Schönberg and Mustafa, *loc. cit.*)]. The difference in behaviour of (I) and (II) towards these reagents is shown by the fact that the resulting product formed in each case from (II), *e.g.*, (V) or (VII*b*), dissociates into its components under the experimental conditions. When the benzene solution of (II) was exposed to sunlight in the presence of oxygen, *o*-dibenzoylbenzene was obtained [compare the rapid absorption by solutions of (I) of atmospheric oxygen to afford *o*-dibenzoylbenzene (Guyot and Catel, *loc. cit.*; Adams and Gold, *loc. cit.*)].

Experimental.—Reaction of 1 : 3-*Diphenyl*iso*benzofuran* (I).—(i) *With nitrosobenzene.* A solution of (I) (Guyot and Catel, *loc. cit.*) (1 g.; 1 mol.) in warm absolute ethyl alcohol (15 c.c.) was heated on a steam-bath with nitrosobenzene (0·8 g.; 2 mols.) and 6 drops of piperidine for 5 minutes. The mixture acquired a blue colour which changed to green and became brown at the end of the reaction. It was left overnight in the ice-chest. The solid that separated was washed with a small amount of cold ethyl alcohol and crystallised from benzene–light petroleum (b. p. 30—50°), m. p. 230° (brown melt) (Found : C, 82·6; H, 5·0; N, 3·5. $C_{26}H_{19}O_2N$ requires C, 82·8; H, 5·1; N, 3·7%). The addition product (III) was soluble in hot ethyl alcohol and benzene and difficultly soluble in cold ethyl alcohol and light petroleum (b. p. 30—50°); it gave a reddish-orange colour when treated with sulphuric acid. When (III) (1 g.) was heated in a stream of dry carbon dioxide for ½ hour at 270° (bath temp.), oily drops collected on the walls of the tube; after 48 hours these solidified and were extracted with hot light petroleum (b. p. 70—80°). The residue after evaporation crystallised from benzene–light petroleum (b. p. 30—50°) as yellow-orange crystals of (I) (m. p. 125—126° and mixed m. p.). The thermal decomposition was repeated in a sealed Pyrex tube which was then chilled as quickly as possible with the help of an ice–salt mixture (cf. Schönberg and Mustafa, *loc. cit.*). The contents of the tube, after being washed several times with light petroleum (b. p. 50—70°), were dissolved in hot acetic acid; on slow cooling, the dimer (VII*a*) was obtained as colourless crystals (identified by m. p. and mixed m. p.).

(ii) *With* p-*nitrosodimethylaniline.* A solution of (I) (1 g.) in warm absolute ethyl alcohol (20 c.c.) was treated with *p*-nitrosodimethylaniline (1·1 g.) and 6 drops of piperidine as described above. The mixture became green, changing to brown at the end of the reaction. It was left overnight at room temperature, and the solid that separated was filtered off, washed with cold methyl alcohol, and crystallised from benzene–light petroleum (b. p. 30—50°); m. p. 220° (red-brown melt). The addition compound (IV) (Found : C, 80·1; H, 5·5; N, 6·4. $C_{28}H_{24}O_2N_2$ requires C, 80·0; H, 5·7; N, 6·6%) was difficultly soluble in methyl alcohol and soluble in hot benzene and xylene.

The same addition compound was obtained when a solution of equimolecular amounts of (I) and *p*-nitrosodimethylaniline in the minimum of dry pyridine was heated for a few minutes on the steam-bath, followed by addition of methyl alcohol (about 3 c.c.).

When (IV) (1 g.) was heated in a stream of dry carbon dioxide, as described for (III), (I) was obtained (m. p. and mixed m. p.).—FOUAD I UNIVERSITY, FACULTY OF SCIENCE, ABBASSIA, CAIRO, EGYPT. [*Received, April 6th,* 1948.]

The Friedel–Crafts Reaction between Succinic Anhydride and 1 : 2-*Diphenylethane.*

By S. D. NICHOLAS and F. SMITH.

THE reaction between succinic anhydride and 1 : 2-diphenylethane (dibenzyl) in the presence of aluminium chloride was examined in order to obtain intermediates for the preparation of basic compounds of possible physiological activity (Smith *et al.*, *J.*, 1946, 524, 526, 528, 665). The reaction afforded a monobasic acid, 1-phenyl-2-β-carboxypropiophenylethane, and a greater proportion of a dibasic acid, 1 : 2-di-(β-carboxypropiophenyl)ethane, which arise by the interaction of the hydrocarbon with one and two moles respectively of succinic anhydride. This is in contrast to diphenyl which combines with one molecular proportion of the succinic anhydride (Hey and Wilkinson, *J.*, 1940, 1030; Weizmann, Bergmann, and Bograchov, *Chem. and Ind.*, 1940, **59**, 402; cf. Haworth, *et al.*, *J.*, 1932, 1125, 1784, 2248, 2720; **1934**, 454).

The dibasic acid was transformed successively into the corresponding ester and amide by the usual procedures. The amide showed a marked tendency to yield a blue compound on being heated just above its m. p. (256°) or even on being heated in glacial acetic acid or especially in formamide solution. The blue substance was not characterised.

1 : 2-*Di-(β-carboxypropiophenyl)ethane and* 1-*Phenyl*-2-β-*carboxypropiophenylethane*.—To a solution of aluminium chloride (10 g.) in nitrobenzene (30 c.c.), a mixture of succinic anhydride (4 g.) and dibenzyl (2 g.) was added at room temperature. After 2 days at room temperature the mixture was poured into ice–water; concentrated hydrochloric acid (20 c.c.) was added, and the mixture subjected to steam distillation to remove nitrobenzene.

Extraction of the dark tarry residue (4·2 g.) with a boiling mixture of glacial acetic acid (50 c.c.) and water (125 c.c.), followed by cooling of the extract, gave a yellow solid (1·9 g.), m. p. 223° with previous softening at 210°. A second extraction with a boiling mixture of glacial acetic acid (70 c.c.) and water (65 c.c.) gave a further 0·4 g. of product.

Recrystallisation of the combined products (2·3 g.) from glacial acetic acid gave 1 : 2-*di-(β-carboxypropiophenyl)ethane* (1·35 g.), m. p. 256° (decomp.) (Found : C, 68·9; H, 6·2; equiv., 190. $C_{22}H_{22}O_6$ requires C, 69·1; H, 5·8%; equiv., 191).

To the mother liquors, obtained from the recrystallisation of the di-acid, excess of water was added. Purification of the precipitated material (0·6 g., m. p. 160—175° with previous softening at 135°) by crystallisation from glacial acetic acid gave a small amount (0·1 g.) of the di-acid, m. p. 245—250°, followed, upon controlled addition of water, by a substance (0·35 g.), m. p. 130° (after further crystallisation either from aqueous acetic acid or carbon tetrachloride), believed to be the monobasic acid, 1-phenyl-2-β-carboxypropiophenylethane (Found : C, 76·4; H, 6·6. Calc. for $C_{18}H_{18}O_3$: C, 76·6; H, 6·4%).

When the dibasic acid (3·2 g.) was boiled for 6 hours with methyl alcohol (375 c.c.) containing sulphuric acid (2 c.c.), the corresponding ester was formed. It was isolated by pouring the reaction mixture into water. Recrystallisation from ethyl alcohol gave the *methyl* ester (3·2 g.), m. p. 119° (Found : C, 70·2; H, 6·1; OMe, 14·6. $C_{24}H_{26}O_6$ requires C, 70·2; H, 6·4; OMe, 15·1%).

Treatment of a solution of the ester (1·5 g.) in methyl alcohol (430 c.c.) with ammonia at 0° followed by several days in the refrigerator gave a crystalline deposit consisting chiefly of the diamide (0·8 g.) (Found : C, 69·6; H, 6·6; N, 5·9. Calc. for $C_{22}H_{24}O_4N_2$: C, 69·3; H, 6·4; N, 7·4%). The amide was purified as far as possible by extraction of unchanged ester with boiling methyl alcohol. Attempts to crystallise it from other solvents such as glacial acetic acid or formamide resulted in the formation of a deep blue solution from which a blue product was obtained. This was particularly noticeable when formamide was used. Rapid crystallisation from dimethylformamide or glacial acetic acid in the presence of charcoal was fairly successful. The substance melts at 238° with the production of a deep blue melt. It is believed that this blue substance, which may arise as a result of further cyclisation, is worthy of further attention.—THE A. E. HILLS LABORATORY, THE UNIVERSITY, EDGBASTON, BIRMINGHAM, 15. [*Received, April 24th,* 1948.]

The Reaction between Acetanilide and Toluene-p-*sulphonyl Chloride in Presence of Aluminium Chloride.*

By H. BURTON and P. F. HU.

ACETANILIDE and toluene-*p*-sulphonyl chloride have been found to react in presence of aluminium chloride in nitrobenzene at 150—160° to give, after hydrolysis, two compounds in widely differing proportions. The minor one, which contained sulphur, appeared to be 4-*amino*-4′-*methyldiphenyl sulphone*, whilst the major product was undoubtedly *NN*′-diphenylacetamidine.

A solution of acetanilide (20 g.; 0·15 mol.) and toluene-*p*-sulphonyl chloride (30 g.; 0·15 mol.) in nitrobenzene (50 c.c.) was stirred mechanically at 150—160° (bath temp.) and treated with powdered aluminium chloride (25 g.) added in portions. Heating and stirring were continued for a further 3 hours, and the resulting dark, viscous solution decomposed with ice and hydrochloric acid. The nitrobenzene was removed completely by steam distillation, and the residual aqueous solution concentrated to *ca.* 200 c.c. Fine needles (*A*) separated from the cooled solution. Evaporation of the filtrate to *ca.* 50 c.c. gave a second crop (*B*) of crystalline material.

Solid (*A*), m. p. 216° after crystallisation from alcohol, was basified to yield 4-*amino*-4′-*methyl*-

diphenyl sulphone (3·7 g.), m. p. 182—183°, after crystallisation from alcohol (Found : C, 62·7; H, 5·2. $C_{13}H_{13}O_2NS$ requires C, 63·1 ; H, 5·2%). Nitrogen and sulphur were shown to be present by Lassaigne's test.

The solid obtained by basifying (*B*) separated from alcohol in prisms (12 g.), m. p. 132—133° (Found : C, 79·3; H, 6·8; N, 12·8. $C_{14}H_{14}N_2$ requires C, 80·0; H, 6·7; N, 13·3%). Busch and Hobein (*Ber.*, 1907, **40**, 4297) give m. p. 132°.

We thank the British Council for a scholarship to one of us (P. F. H.).—THE UNIVERSITY, LEEDS, 2. [*Received, April 28th,* 1948.]

The Mechanism of the Formation of Diphenyl Sulphoxide from Phenylmagnesium Bromide and Thiophen-2-sulphonyl Chloride. By H. BURTON and P. F. HU.

IN order to explain the production of diphenyl sulphoxide from phenylmagnesium bromide and thiophen-2-sulphonyl chloride, in boiling benzene, Burton and Davy (*J.*, 1948, 528) suggested that the following intermediate reaction might occur: $Ar{\cdot}SO_2{\cdot}MgBr + MgPhBr \longrightarrow Ar{\cdot}MgBr + Ph{\cdot}SO_2{\cdot}MgBr$. If one assumed that this reaction occurred exclusively, the formation of 1 molecule of diphenyl sulphoxide from 1 molecule of thiophen-2-sulphonyl chloride would require 3 molecules of phenylmagnesium bromide, owing to the following reactions taking place :

(i) $Ar{\cdot}SO_2Cl + MgPhBr \longrightarrow Ar{\cdot}SO_2{\cdot}MgBr + PhCl$;
(ii) $Ar{\cdot}SO_2{\cdot}MgBr + MgPhBr \longrightarrow Ar{\cdot}MgBr + Ph{\cdot}SO_2{\cdot}MgBr$;
(iii) $Ph{\cdot}SO_2{\cdot}MgBr + MgPhBr \longrightarrow Ph_2SO + (MgBr)_2O$ (see Burton and Davy, *loc. cit.*).
(Ar = 2-thienyl)

The reaction mixture would clearly contain 1 mol. of 2-thienylmagnesium bromide which should be capable of being detected by, for example, carbonation, since thiophen-2-carboxylic acid would be produced. Our preliminary experiments in this direction indicated that carbonation of the 2-thienylmagnesium bromide was slow, but, after treatment of such a reaction mixture with dry carbon dioxide for 20 hours, we were able to isolate about 30% of the calculated amount of the thiophen-2-carboxylic acid with little or no benzoic acid. We conclude, therefore, that the above mechanism accounts satisfactorily for our previous results.

Experimental.—Thiophen-2-sulphonyl chloride (9·1 g.; 0·05 mol.) in benzene (75 c.c.) was added slowly with stirring to cold, ethereal phenylmagnesium bromide (0·15 mol.), and the mixture then refluxed for 20 hours. Dry carbon dioxide was then passed into the mixture, cooled to room temperature, for 20 hours with stirring; ether was added at intervals to maintain a constant volume. Decomposition with ice and 50% sulphuric acid and extraction of the aqueous phase with 3 successive portions of benzene gave a combined ether–benzene extract which was washed with cold water, and then extracted with 2N-sodium hydroxide (40 c.c.). Acidification of the alkaline extract gave, after extraction with ether and evaporation, 2 g. (31%) of thiophen-2-carboxylic acid, m. p. 124—126° after crystallisation from water (Found : S, 25·1. Calc. for $C_5H_4O_2S$: S, 25·0%). The acid was further characterised by conversion through the acid chloride into the amide, colourless needles from water, m. p. 175—176°. In another experiment the thiophen-2-carboxylic acid, m. p. 124—126°, was found to contain S, 23·1% (equivalent to 92·4% of the acid).

We thank the Universities China Committee for financial assistance to one of us (P. F. H.).—THE UNIVERSITY, LEEDS, 2, and KING'S COLLEGE OF HOUSEHOLD AND SOCIAL SCIENCE, W.8. [*Received, April 28th,* 1948.]