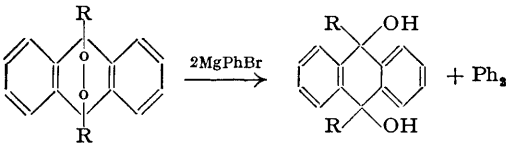
# NOTES.

*Reactions of Grignard Solutions. Part II. Action of the Grignard Reagent on Photo-peroxides of* 9 : 10-*Diarylanthracene.* By AHMED MUSTAFA.

DUFRAISSE (*Bull. Soc. chim.*, 1933, [iv], **53**, 789) has obtained 5 : 12-dihydroxy-5 : 6 : 11 : 12-tetraphenyl-5 : 12-dihydronaphthacene by the action of Grignard reagents on 5 : 6 : 11 : 12-tetraphenylnaphthacene dioxide, an *isomerisation product* obtained by the action of magnesium iodide on an ethereal solution of the photo-peroxide of 5 : 6 : 11 : 12-tetraphenylnaphthacene (cf. Dufraisse, *loc. cit.*; Bergmann and Maclean, *Chem. Reviews*, 1941, **28**, 387). All attempts to rearrange the photo-peroxides of 9 : 10-diphenylanthracene (I*a*) in an analogous manner have failed (Dufraisse and Le Bras, *Bull. Soc. chim.*, 1937, [v], **4**, 349).

The photo-peroxide (I*a*) of 9 : 10-diphenylanthracene with phenylmagnesium bromide, in ether–benzene gives, after decomposition with ammonium chloride, 9 : 10-dihydroxy-9 : 10-diphenyl-9 : 10-dihydroanthracene (II*a*) in almost quantitative yield together with diphenyl, whereas (I*a*) is recovered unchanged when shaken with an aqueous solution of ammonium chloride for three hours at room temperature (cf. the action of water in dioxan in the presence of sulphuric acid; Pinnazi, *Compt. rend.*, 1947, **225**, 1012). 9 : 10-Dihydroxy-9 : 10-di-*p*-tolyl- (II*b*) and 9 : 10-dihydroxy-9 : 10-di-*m*-tolyl-

dihydroanthracene (II*c*) were obtained similarly from the photo-peroxides of 9 : 10-di-*p*-tolyl- (I*b*) and 9 : 10-di-*m*-tolyl-anthracene (I*c*), respectively.




(I*a* : R = Ph; I*b* : R = *p*-$C_6H_4Me$; I*c* : R = *m*-$C_6H_4Me$). (II*a*, *b*, *c*.)

This is an example of the breaking of the linkage by the action of Grignard reagent, resulting in reduction (cf. Crawford, *J. Amer. Chem. Soc.*, 1935, **57**, 2000; Kharasch and Weinhouse, *J. Org. Chem.*, 1936, **1**, 209).

*Action of Phenylmagnesium Bromide.*—(a) *On* 9 : 10-*diphenylanthracene* (*photo-*)*peroxide.* An ethereal solution of phenylmagnesium bromide [prepared from magnesium (1·8 g.), bromobenzene (18·8 g.), and dry ether (100 c.c.)] was filtered and divided into two portions. To one portion, (I*a*) (1·5 g.) and dry benzene (30 c.c.) were added. To the second portion, only dry benzene (30 c.c.) was added. The two portions were then boiled under reflux for two hours and kept overnight at room temperature, and then decomposed with cold aqueous ammonium chloride solution and extracted with ether. The ethereal solutions were washed with water, dried ($Na_2SO_4$), and evaporated. The oily residue obtained from the first portion was extracted several times with light petroleum (b. p. 30—50°); the insoluble solid material obtained after thorough washing with light petroleum crystallised from benzene in colourless crystals, m. p. 255—256° (1·2 g.; *ca.* 85%); it was 9 : 10-dihydroxy-9 : 10-diphenyldihydroanthracene (II*a*) (m. p., mixed m. p., and blue colour with concentrated sulphuric acid) (Found: C, 85·6; H, 5·4. Calc. for $C_{26}H_{20}O_2$: C, 85·7; H, 5·4%). The light-petroleum extract gave, on slow evaporation, diphenyl as colourless crystals, m. p. 71° (0·74 g.).

The oily residue obtained from the evaporation of the second ethereal solution solidified when cooled and scratched and was then recrystallised from light petroleum (b. p. 50—60°), giving diphenyl as colourless crystals, m. p. 71° (0·23 g.).

(b) *On* 9 : 10-*di*-p-*tolylanthracene* (*photo-*)*peroxide* (I*b*). (I*b*) (Willemart, *Bull. Soc. chim.*,1 937, [v], **4**, 510) (1·5 g.), when similarly treated, gave 9 : 10-dihydroxy-9 : 10-di-*p*-tolyl-9 : 10-dihydroanthracene (II*b*) as colourless crystals, m. p. 273° from benzene (m. p., mixed m. p., and colour reaction with sulphuric acid) (Found : C, 85·8, H, 6·0. Calc. for $C_{28}H_{24}O_2$ : C, 85·7; H, 6·1%). Ingold and Marshall (*J.*, 1926, 3080) gave m. p. 275° for (II*b*).

(c) *On* 9 : 10-*di*-m-*tolylanthracene* (*photo-*)*peroxide* (I*c*). Similarly, (I*c*) (Willemart, *loc. cit.*) (1·5 g.) afforded 9 : 10-dihydroxy-9 : 10-di-*m*-tolyl-9 : 10-dihydroanthracene (II*c*) as colourless crystals (from toluene), m. p. 247° (m. p., mixed m. p., and colour reaction with sulphuric acid) (Found : C, 85·6; H, 6·2).—Faculty of Science, Fouad I University, Abbassia, Cairo, Egypt. [*Received, November 17th*, 1948.]

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*The Preparation of Diacridyl by treating 5-Chloroacridine with Chromous Sulphate.* By Richard Royer.

The reduction of 5-chloroacridine by chromous sulphate has been investigated. The use of chromous chloride has been recommended for reducing iminochlorides to Schiff bases by von Braun and Rudolph (*Ber.*, 1934, **67**, 269, 1735), and, as 5-chloroacridine may be considered a vinylogous iminochloride, it was anticipated that this method of reduction would yield acridine. However, no appreciable quantity of acridine or acridan was formed, but diacridyl was produced in almost quantitative yield.

A 0·1N-chromous sulphate solution in 0·1N-sulphuric acid was prepared by the simplified method of Lingane and Pectok (*Analyt. Chem.*, 1948, **20**, 425). This solution (100 ml.) was added, in an atmosphere of hydrogen, to a solution of 5-chloroacridine (0·50 g.; 0·0023 mole) in glacial acetic acid (9 ml.) at 20°. The change in colour from blue to green was immediate. After 30 minutes, concentrated sulphuric acid (2 ml.) and potassium dichromate (0·85 g.) were added, and the mixture was boiled for 20 minutes. After the mixture had been cooled, the solid was collected, washed thoroughly with water, and decomposed by aqueous ammonia, giving diacridyl (0·40 g.; 96%) [Found (after crystallisation from pyridine): C, 87·3; H, 4·4. Calc. for $C_{26}H_{16}N_2$: C, 87·6; H, 4·5%—microanalysis by The Wellcome Chemical Works, Dartford]. The product did not melt below 360° and was insoluble in alcohol (imparting no fluorescence to the wash-liquor); when potassium iodide was added to its solution in 0·5N-hydrochloric acid, the characteristic red iodide of diacridyl separated.—Wellcome Research Institution, London, N.W.1. [*Received, December 9th*, 1948.]

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*Relative Rates of Hydrogenolysis.* By J. G. M. Bremner and R. K. F. Keeys.

The hydrogenolysis of furfuraldehyde to sylvan at atmospheric pressure in presence of a copper catalyst is inhibited by the presence of alkali, furfuryl alcohol being the main product formed (Bremner and Keeys, *J.*, 1947, 1068). The behaviour of acetophenone under similar conditions has now been examined. It has been found that a copper catalyst which leads to furfuryl alcohol in good yield does not show the same selectivity in the hydrogenation of acetophenone. The reaction does not stop when phenylmethylcarbinol is formed, but hydrogenolysis sets in with the formation of ethylbenzene and water. Thus 1·96 moles of hydrogen per mole of acetophenone were absorbed on passing the ketone at a

space velocity * of 0·32 hour$^{-1}$, with a 5·5-molar ratio of hydrogen, over the copper catalyst at 235°. Only a trace (1%) of unchanged ketone, estimated by oximation, was present in the product which was in two layers. Distillation gave a water–ethylbenzene fraction, followed by the main ethylbenzene fraction at 135°, whilst only 8% of higher-boiling material remained.

Since it has already been shown (*loc. cit.*) that those catalysts which reduce furfuraldehyde to sylvan do not convert acetone into propane, the following sequence (cf. Adkins, " Reactions of Hydrogen," Univ. of Wisconsin Press, 1937, p. 70) with regard to rate of reaction with hydrogen is observed: acetophenone > furfuraldehyde ≫ acetone. If it be assumed that ions of the type, $^+$CHPhMe, $C_4H_3O{\cdot}CH_2^+$, and $Pr^{i+}$, are intermediates in these hydrogenolysis reactions (Bremner, *Research*, 1948, **1**, 281), their respective resonance energies will be in this, the expected, sequence.—IMPERIAL CHEMICAL INDUSTRIES LIMITED, BILLINGHAM DIVISION, BILLINGHAM, CO. DURHAM. [*Received, December 16th*, 1948.]

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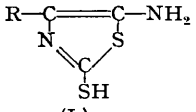
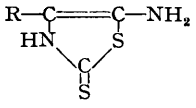
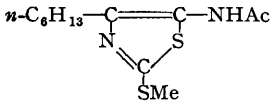
*Thiol–thione Tautomerism of 5-Amino-2-mercaptothiazoles.* By E. S. STERN.

DATA for the ultra-violet-light absorption of 5-amino-2-mercaptothiazoles (I, I*a*) in neutral and alkaline solution (see table) published recently (Cook *et al.*, *J.*, 1947, 1598; 1948, 201, 2031) permit the interpretation of an interesting case of functional-group isomerism influenced by the substituent in the 4-position of the thiazole nucleus.

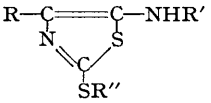

(I.)


(I*a*.)


(II.)

Of the two possible forms (I and I*a*), the thiol form (I) may be assumed to be favoured in alkaline solution. When R = H or an alkyl group (*e.g.*, *n*-$C_6H_{13}$, or CHEt$Bu^n$), the ammoniacal solution of the thiazoles shows a light-absorption maximum at about 3040 A. This maximum ($\lambda_{max.}$ 2990 A.) is also observed for 5-acetamido-2-methylthio-4-*n*-hexylthiazole (II), a compound presumably existing entirely in the " thiol " form, in alcoholic solution. The absorption spectra of alcoholic solutions of 5-amino- and 5-acetamido-2-mercapto-4-alkylthiazoles, however, differ markedly from those of alkaline solutions and show maxima at about 3380 A., and at 3370 A., respectively. It may be concluded, therefore, that in alcoholic solution the thione form (I*a*) predominates.

*Light Absorption Properties of Aminomercaptothiazoles.*



| | | | | Neutral solution. | | Alkaline solution. | |
|---|---|---|---|---|---|---|---|
| Ref. | R. | R′. | R″. | $\lambda_{max.}$. | ε. | $\lambda_{max.}$. | ε. |
| *a* | H | H | H | 2280 A. | 4,500 | Unstable | |
| | | | | 3380 | 10,700 | | |
| *b* | *n*-$C_6H_{13}$ | H | H | 3340 | 11,200 | 3040 A. | 5,500 |
| *b* | CHEt$Bu^n$ | H | H | 3390 | 11,500 | 3040 | 7,500 |
| *c* | Ph | H | H | 2230 | 12,500 | 2230 | 18,000 |
| | | | | 2810 | | 3060 | 12,000 |
| | | | | 2900 | 8,500 | | |
| | | | | 3000 | | | |
| *b* | *n*-$C_6H_{13}$ | Ac | H | 3370 | 16,000 | | |
| *b* | *n*-$C_6H_{13}$ | Ac | Me | 2500 | 3,600 | | |
| | | | | 2560 | 3,600 | | |
| | | | | 2990 | 12,000 | | |

References: *a*, *J.*, 1948, 201; *b*, *J.*, 1948, 2031; *c*, *J.*, 1947, 1598.

5-Amino-2-mercapto-4-phenylthiazole (I; R = Ph), on the other hand, has its light-absorption maximum of longest λ in dioxan and in alkaline solution at 3000 A. and at 3060 A., respectively, and thus appears to exist in the thiol form (I) in neutral solution.

The fact that these differences in light absorption are accompanied by great differences in melting point and other physical properties, and by differences in reactivity towards methylating agents (*e.g.*, diazomethane) in alcoholic solution, lends support to the view that this is a case of tautomerism in which the substituent at the 4-position plays a decisive role in determining the final form assumed by the ring system, and which may be explained in the following terms. The thiazole ring system is now generally accepted as being aromatic in character (see Erlenmeyer *et al.*, *Helv. Chim. Acta*, 1948, **31**, 1978) and probably exists in the form of a resonance hybrid in which the classical single and double bonds interact to a large extent (cf. Metzger and Pullman, *Compt. rend.*, 1948, **226**, 1613). In the thiazoline structure (I*a*) there are two single bonds between $C_{(4)}$ and $C_{(2)}$, and this tautomer would not be expected to conjugate with a substituent at $C_{(4)}$; in the resonating thiazole structure (I), on the other hand, there should

* Space velocity refers to the volume of acetophenone fed per unit bulk volume of catalyst space per hour.

be no obstacle to conjugation with a substituent at $C_{(4)}$, and the structure (I) should be favoured by $C_{(4)}$-substituents with great conjugating power. The conjugating power of the phenyl substituent is evidently sufficient, and that of an alkyl substituent is insufficient, to force the hetero-ring into the thiazole form (I) capable of conjugation. The author thanks Sir Ian Heilbron and Dr. A. H. Cook for their kind interest and encouragement.—IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W.7. [*Received, December 21st*, 1948.]

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*Some Guanidine and Diguanide Derivatives.* By RICHARD ROYER.

IN the course of studies on the relation between chemical constitution and antibacterial properties, the need arose for a series of aryl-guanidines and -diguanides having different areas of flat surface. This involved the preparation of the following compounds not previously described, *viz.*, 2-*anthryl*- and 3-*acridyl-guanidine* and N$^1$-2-*anthryl*-, N$^1$-6-*quinolyl*-, and N$^1$-3-*acridyl-diguanide*. 2-Aminoanthracene was treated with methyl*iso*thiourea sulphate, and 3-aminoacridine was condensed with cyanamide, to form the corresponding guanidines. The diguanides were prepared by treating the appropriate amine hydrochlorides with dicyandiamide.

2-*Anthrylguanidine*.—2-Aminoanthracene (1·0 g.), methyl*iso*thiourea sulphate (3·7 g.; 5 equivs.) and a trace of copper sulphate were heated in *p*-cresol (5 g.) at 200—205° for 45 minutes, whereafter evolution of methanethiol ceased. The cooled mass was extracted with ether to remove *p*-cresol, and the residue was basified with excess of 60% sodium hydroxide solution. The mixture of bases was made acid to litmus with N-acetic acid, boiled, and filtered, and the residue extracted with boiling water until no further solid was obtained on basifying the extract. The combined filtrates, on basification with 60% sodium hydroxide solution, gave 0·64 g. (51%). Crystallisation from alcohol (75 parts) yielded 2-*anthrylguanidine* as yellow crystals, m. p. 215° (decomp.) (Found : C, 76·0; H, 5·6; N, 17·8. $C_{15}H_{13}N_3$ requires C, 76·55; H, 5·6; N, 17·85%). Solutions of the base do not display the green fluorescence of 2-aminoanthracene; the mono-ion is colourless, the solution fluorescing violet. The hydrochloride is moderately soluble in cold water.

2-Naphthylguanidine, similarly prepared in 30% yield, had m. p. 143·5° (from benzene). Arndt and Rosenau (*Ber.*, 1917, **50**, 1261) gave m. p. 140°.

3-*Acridylguanidine*.—3-Aminoacridine dihydrochloride (2·7 g.) and cyanamide (3·7 g.) in absolute alcohol (15 ml.) were heated for 7 hours in a sealed tube in a bath at 130—135°. The dark mass was evaporated to dryness, the residue basified with 60% sodium hydroxide solution, and the resulting tar washed with water and dried (in a desiccator; KOH). The tar was extracted with N-acetic acid, and the extract made neutral to litmus with ammonia, liberating a red oil (*A*). The liquor was separated and made alkaline to Orange-II paper with 60% sodium hydroxide solution, precipitating a tar. The oil (*A*) was submitted to the above process repeatedly until final basification was not productive. The precipitated tars were collected and crystallised twice from alcohol, giving 0·5 g., m. p. 203° (decomp.) (15%). Recrystallisation from alcohol (15 parts) yielded 3-*acridylguanidine* as solvated yellow crystals, m. p. 206° (decomp.) (Found : C, 67·1; H, 6·8; N, 18·2. $C_{14}H_{12}N_4,1\frac{1}{2}C_2H_6O$ requires C, 66·8; H, 6·9; N, 18·4%). The base does not fluoresce in solution, and the mono-ion is yellow, displaying a faint violet fluorescence in dilute solution (3-aminoacridine shows an intense green fluorescence in solution and has a red mono-ion). The acetate and hydrochloride are freely soluble in water.

N$^1$-2-*Anthryldiguanide*.—2-Aminoanthracene hydrochloride (6·8 g.), dicyandiamide (2·5 g.; 1 equiv.), and alcohol (30 ml.) were heated for 7 hours in a sealed tube in a bath at 125—130°. The solid was washed with alcohol and shaken in a stoppered flask with excess of 60% sodium hydroxide solution; the resulting mixture of bases was dried and extracted with boiling toluene (100 ml.) to remove unchanged 2-aminoanthracene. The residue was extracted with boiling alcohol (3 l.), and the extract concentrated to crystallising-point, yielding the required base (4·2 g.; 51%). Recrystallisation from alcohol (400 parts) gave N$^1$-2-*anthryldiguanide* as pale yellow crystals, m. p. 214° (decomp.) (Found : C, 69·4; H, 5·5; N, 25·1. $C_{16}H_{15}N_5$ requires C, 69·25; H, 5·5; N, 25·25%). Solutions of the base do not fluoresce and the mono-ion is colourless. The hydrochloride is sparingly soluble in cold water. Attempts to effect the reaction in water, glycerol, or ethylene glycol were less successful.

N$^1$-6-*Quinolyldiguanide*.—6-Aminoquinoline (7·2 g.), dicyandiamide (4·2 g.; 1 equiv.), and 3N-hydrochloric acid (30 ml.) were heated under reflux for 2 hours; after concentration of the solution to one-third of its volume, the addition of alcohol (120 ml.) precipitated the hydrochloride (6·5 g.). To a solution of this salt (2·65 g.) in water (8 ml.) was added 60% sodium hydroxide solution (4·5 ml.), precipitating an oil which quickly solidified (1·83 g., 34%). Crystallisation from alcohol (3 parts) gave N$^1$-6-*quinolyldiguanide* as pale buff crystals, m. p. 188° (decomp.) (Found : C, 57·45; H, 5·3; N, 36·6. $C_{11}H_{12}N_6$ requires C, 57·9; H, 5·3; N, 36·8%). The base is soluble in *ca.* 20 parts of cold and 4 parts of boiling water, or in 10 parts of cold alcohol; it is sparingly soluble in ether or benzene. The solution in 3N-hydrochloric acid fluoresces bright yellow in ultra-violet light.

N$^1$-3-*Acridyldiguanide*.—3-Aminoacridine (2·2 g.), dicyandiamide (1·0 g.; 1 equiv.) and 2N-hydrochloric acid (8·8 ml.) were heated under reflux for 2 hours, and the solution cooled to 60°. Sodium hydrogen carbonate (3·3 g.) in water (10 ml.) then precipitated a tar which was extracted with water (at 60°) until it solidified, leaving unchanged 3-aminoacridine (0·95 g.). The combined filtrates were acidified and boiled to expel carbon dioxide, and the crude base was precipitated by the addition of excess 60% sodium hydroxide solution. A second sodium hydrogen carbonate treatment (as above) removed a further trace of 3-aminoacridine. The precipitated base was then crystallised from alcohol (60 parts), giving yellow crystals of N$^1$-3-*acridyldiguanide*, m. p. 202° (decomp.) (yield, 13%) (Found : C, 64·8; H, 5·1; N, 29·9. $C_{15}H_{14}N_6$ requires C, 64·7; H, 5·1; N, 30·2%). Solutions of the base do not fluoresce and the mono-ion is yellow. The yield was not improved by prolonging the reaction time or by using a two-fold excess of dicyandiamide.

The dissociation constants of these bases were determined potentiometrically in 50% alcohol at 20° by Mr. J. N. Phillips, M.Sc., University of Sydney, by whose kind permission they are reproduced here.

*viz.*: 2-naphthyl- 10·7, 2-anthryl- 11·0, and 3-acridyl-guanidine 10·3; $N^1$-2-anthryl- 10·4, and $N^1$-6-quinolyl-diguanide 10·7. It was not possible to obtain an accurate figure for $N^1$-3-acridyldiguanide because of a strong tendency to form micelles, even in dilute solution.

The author thanks Dr. A. Albert for help and criticism and Miss J. Fildes, B.Sc., for microanalyses.—THE UNIVERSITY, SYDNEY. [*Received, January 8th,* 1949.]

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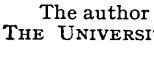
*Some 2-Thienyl Alkyl Sulphones.* By J. CYMERMAN and J. L. LOWE.

THE antibacterial properties of many *p*-substituted phenyl alkyl sulphones are well known, and preliminary model experiments directed towards the synthesis of thiophen analogues, *e.g.*, [I; R = $NH_2$, $CH_2{\cdot}NH_2$, or $C(:NH){\cdot}NH_2$; R″ = alkyl or aralkyl] have now been carried out.



(I.)

Several aryl thienyl sulphones have been described (*e.g.*, Bambas, *J. Amer. Chem. Soc.*, 1945, **67**, 668; Burton and Davy, *J.*, 1948, 525), and Burton and Davy (*loc. cit.*) also prepared 2-thienyl methyl sulphone. This compound was made independently in this laboratory, along with a series of homologues (I; R′ = H; R″ = alkyl or aralkyl), which is listed in the table. The method used in each case was the alkylation of sodium thiophen-2-sulphinate. Attempts to prepare the hexadecyl compound gave an unidentified solid, m. p. 35°.

Decomposition of an aqueous solution of thiophen-2-sulphinic acid, catalysed by hydriodic acid, afforded *di*(2-*thienyl*) *disulphoxide*, m. p. 46—47°.

The molecular refractivities of the liquid sulphones were determined, using a micro-method, accurate to about 1%, to determine the densities. The figures (see table) are in fair agreement with those calculated from the atomic refractivities of sulphur, in its several valency states, given by Strecker and Spitaler (*Ber.*, 1926, **59**, 1754).

| Alkyl Group. | Yield, %. | B. p./mm. | $n_D^t$. | $d_4^t$. | Formula. | $[R_L]_D$. Found. | $[R_L]_D$. Calc. | Analysis, %. Found. C. | Found. H. | Reqd. C. | Reqd. H. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Methyl ..... | 36 | (m. p. 47°) | — | — | $C_5H_6O_2S_2$ | — | — | 37·5 | 3·4 | 37·05 | 3·7 |
| *Ethyl* ..... | 27 | 120°/2·5 | 1·5507 (18°) | 1·297 (18°) | $C_6H_8O_2S_2$ | 43·39 | 43·18 | 40·95 | 4·25 | 40·9 | 4·55 |
| n-*Propyl* ..... | 70 | 153—154°/6·5 | 1·5404 (20°) | 1·259 (20°) | $C_7H_{10}O_2S_2$ | 47·33 | 47·80 | 44·25 | 5·3 | 44·5 | 5·25 |
| n-*Butyl* ..... | 29 | 163—165°/3 | 1·5369 (15°) | 1·199 (15°) | $C_8H_{12}O_2S_2$ | 52·98 | 52·42 | 47·1 | 6·05 | 47·1 | 5·9 |
| n-*Amyl* ..... | 33 | 162—163°/2 | 1·5282 (17°) | 1·181 (17°) | $C_9H_{14}O_2S_2$ | 56·80 | 57·04 | 49·5 | 6·05 | 49·55 | 6·4 |
| n-*Hexyl* ..... | 30 | 160°/2 | 1·5230 (15°) | 1·176 (15°) | $C_{10}H_{16}O_2S_2$ | 61·20 | 61·66 | 51·7 | 7·0 | 51·7 | 6·9 |
| 4-*Nitrobenzyl* | 9 | (m. p. 177°) | — | — | $C_{11}H_9O_4NS_2$ | — | — | N 5·3 | — | N 4·95 | — |

*Thiophen-2-sulphinic Acid* (*cf.* Smiles and Bere, *J.*, 1924, 2361).—Thiophen-2-sulphonyl chloride (9·15 g.) (Steinkopf and Hopner, *Annalen*, 1933, **501**, 174) in acetone (10 c.c.) was slowly added to a vigorously stirred solution of sodium sulphite heptahydrate (25·2 g.) in water (120 c.c.) at 60°. The solution was maintained at pH 8—9 by suitable additions of solid sodium hydrogen carbonate, and stirred at 60° for 2 hours after the addition of sulphonyl chloride was complete. After cooling, the solution was acidified with 2N-sulphuric acid and extracted with ether. The ethereal extract was shaken with dilute sodium hydrogen carbonate solution (150 c.c.), and the aqueous solution of sodium thiophen-2-sulphinate thus obtained (0·041 mol., 81% of theory; amount estimated in an aliquot part by acidifying, extracting the sulphinic acid with chloroform, and titrating with standard sodium hydroxide solution) was used in subsequent preparations.

*Preparation of Sulphones.*—A solution (pH 8—9) of sodium thiophen-2-sulphinate (0·02 mol.) in water (70 c.c.) was heated under reflux for 12—18 hours with the alkyl halide (0·6 mol.) and sufficient alcohol to render the hot solution homogeneous. Excess of alkyl halide and alcohol were distilled off, and the sulphones isolated by ether extraction. The crude products were usually purified by vacuum-distillation, except the methyl and *p*-nitrobenzyl compounds, which were crystallised from aqueous alcohol.

*Di-*(2-*thienyl*) *Disulphoxide.*—A solution of sodium thiophen-2-sulphinate (0·01 mol.) in water (35 c.c.) was acidified with 2N-sulphuric acid, and 10% hydriodic acid (0·1 c.c.) was added. The mixture was set aside at room temperature for 3 days, whereupon white crystals gradually separated. Extraction with ether, and removal of solvent from the washed (sodium hydrogen carbonate) and dried extract, afforded a residue of di-(2-thienyl) disulphoxide, crystallising from aqueous alcohol in white needles, m. p. 46—47° (0·31 g.; 36%) (Found: C, 36·55; H, 2·2. $C_8H_6O_2S_4$ requires C, 36·65; H, 2·3%).

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