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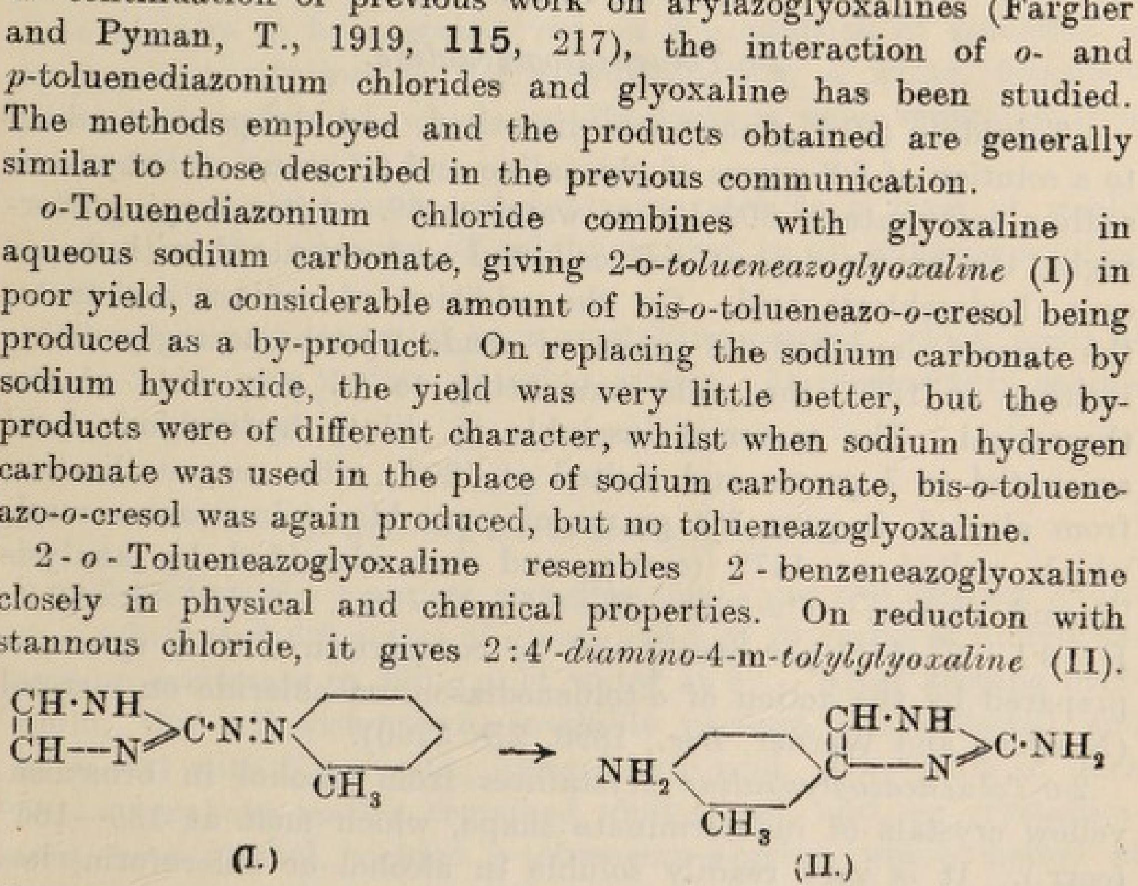
CLVI.—o- *and* p-*Tolueneazoglyoxalines.*

By Frank Lee Pyman and Leonard Allan Ravald.

In continuation of previous work on arylazoglyoxalines (Fargher and Pyman, T., 1919, **115**, 217), the interaction of *o*- and *p*-toluenediazonium chlorides and glyoxaline has been studied. The methods employed and the products obtained are generally similar to those described in the previous communication.

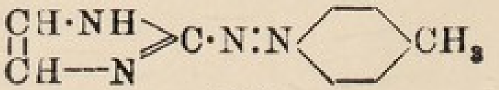
o-Toluenediazonium chloride combines with glyoxaline in aqueous sodium carbonate, giving 2-o-*tolueneazoglyoxaline* (I) in poor yield, a considerable amount of bis-*o*-tolueneazo-*o*-cresol being produced as a by-product. On replacing the sodium carbonate by sodium hydroxide, the yield was very little better, but the by-products were of different character, whilst when sodium hydrogen carbonate was used in the place of sodium carbonate, bis-*o*-tolueneazo-*o*-cresol was again produced, but no tolueneazoglyoxaline.

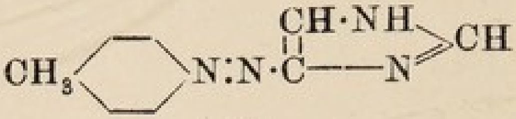
2-*o*-Tolueneazoglyoxaline resembles 2-benzeneazoglyoxaline closely in physical and chemical properties. On reduction with stannous chloride, it gives 2:4′-*diamino*-4-m-*tolylglyoxaline* (II).



(I.) (II.)

The combination of *p*-toluenediazonium chloride with glyoxaline in aqueous sodium carbonate leads to the formation of 2-p-*tolueneazoglyoxaline* (III) in good yield, together with a small amount of an isomeride, doubtless 4-p-*tolueneazoglyoxaline* (IV), and a quantity of *p*-tolueneazo-*p*-cresol. We had expected that


(III.)


(IV.)

2-*p*-tolueneazoglyoxaline would resemble 2-*p*-bromobenzeneazoglyoxaline in giving a good yield of 2-aminoglyoxaline when reduced with stannous chloride under the conditions employed by Fargher and Pyman (*loc. cit.*, p. 244), but this was not the case, 2-aminoglyoxaline being produced in a yield of less than 15 per cent. of the theoretical, together with *p*-toluidine, guanidine, ammonia, and unidentified products. When 2-*p*-tolueneazoglyoxaline is reduced with zinc dust and acetic acid under the conditions previously employed for the reduction of 2-benzeneazoglyoxaline (*ibid.*, p. 241), *p*-toluidine and glycocyamidine were obtained in yields amounting to 97 and 42 per cent. of the theoretical respectively.

EXPERIMENTAL.

2-o-*Tolueneazoglyoxaline*.

o-Toluidine (10·7 grams) was diazotised, and the product added to a solution of 6·8 grams of glyoxaline and 20 grams of anhydrous sodium carbonate in 500 c.c. of water at 5°. After keeping overnight, the brown deposit was collected and extracted with 5 per cent. hydrochloric acid. On the addition of sodium carbonate, the extract deposited 4·8 grams of crude 2-*o*-tolueneazoglyoxaline melting at 165°, the yield amounting to 26 per cent. of the theoretical. The material insoluble in dilute hydrochloric acid amounted to 7 grams and melted at 120°; after recrystallisation from alcohol, it gave 3·3 grams of pure bis-*o*-tolueneazo-*o*-cresol, which melted at 147° (corr.), and was identified by analysis [Found (mean): C=72·4; H=6·0; N=16·6. Calc.: C=72·2; H=6·1; N=16·9 per cent.] and by comparison with a specimen prepared by the action of *o*-toluenediazonium chloride on *o*-cresol (Noelting and Werner, *Ber.*, 1890, **23**, 3260).

2-o-*Tolueneazoglyoxaline* crystallises from alcohol in brownish-yellow crystals of indeterminate shape, which melt at 185—186° (corr.). It is very readily soluble in alcohol or chloroform, less readily so in ether or benzene (Found: C=64·6, 64·4; H=5·4, 5·7; N=30·1. $C_{10}H_{10}N_4$ requires C=64·5; H=5·4; N=30·1 per cent.).

Reduction of 2-o-*Tolueneazoglyoxaline with Stannous Chloride. Isolation of* 2 : 4′-*Diamino*-4-m-*tolylglyoxaline.*

Two grams of 2-*o*-tolueneazoglyoxaline were dissolved in 20 c.c. of hot 2·5 per cent. hydrochloric acid and mixed with 12 c.c. of stannous chloride (40 per cent. w/v) in hydrochloric acid. On cooling the solution and adding 20 c.c. of concentrated hydrochloric acid, 4 grams of a crystalline stannichloride were deposited, which, after the removal of the tin, gave 2 grams of 2 : 4′-diamino-4-*m*-tolylglyoxaline dihydrochloride, that is, 67 per cent. of the theoretical yield.

2 : 4′-*Diamino*-4-m-*tolylglyoxaline dihydrochloride* separates from dilute hydrochloric acid in microscopic needles, which form a white, spongy mass. After drying at 50°, it contains $1H_2O$. It is readily soluble in cold, very readily so in hot, water [Found (in substance dried at 50°): C = 43·0; H = 5·8; N = 19·9, 20·1; Cl = 25·7; H_2O = 6·9. $C_{10}H_{12}N_4,2HCl,H_2O$ requires C = 43·0; H = 5·8; N = 20·1; Cl = 25·5; H_2O = 6·5 per cent.].

Its reactions with potassium permanganate, sodium nitroprusside, sodium diazobenzene-*p*-sulphonate, and nitrous acid are similar to those of the lower homologue (T., 1919, **115**, 240). The base appears to be unstable, for, on the addition of ammonia to an aqueous solution of the dihydrochloride, a white, flocculent precipitate is formed, which rapidly darkens when separated from the solution.

The sparingly soluble *sulphate* separates as a mass of woolly needles on the addition of sulphuric acid to an aqueous solution of the salt.

The *dipicrate* separates as a crystalline powder, which melts at about 210° (corr.) after sintering earlier. It is sparingly soluble in boiling water.

2- *and* 4-p-*Tolueneazoglyoxalines.*

p-Toluidine (10·7 grams) was diazotised, and the product added to a solution of 6·8 grams of glyoxaline and 20 grams of anhydrous sodium carbonate in 500 c.c. of water at 5°. After keeping overnight, the yellowish-brown, insoluble product was collected and extracted with 5 per cent. hydrochloric acid. One gram of dark red, amorphous matter remained undissolved, and, on crystallisation from alcohol, yielded *p*-tolueneazo-*p*-cresol, which melted at 112° (corr.), and was identified by analysis (Found: C = 73·7; H = 6·8; N = 12·5. Calc.: C = 74·3; H = 6·3; N = 12·4 per cent.) and by comparison with a specimen prepared by the action of *p*-toluenediazonium chloride on *p*-cresol (Noelting and Kohn, *Ber.*, 1884, **17**, 354). The hydrochloric acid extract was basified with sodium carbonate, and deposited 15·2 grams of the mixed tolueneazoglyoxalines melting at 220°, that is, 86 per cent. of the theoretical yield. On recrystallisation from alcohol, 11·6 grams of 2-*p*-tolueneazoglyoxaline were obtained in a pure state, and small crops of impure material. From the final filtrate, 4-*p*-tolueneazoglyoxaline was isolated in the form of its hydrochloride.

2-p-*Tolueneazoglyoxaline* crystallises from alcohol in yellow leaflets, which melt at 235° (corr.). It is soluble in boiling alcohol to the extent of rather less than 5 per cent. (Found: C=64·1, 64·4; H=5·6, 5·6; N=30·1. $C_{10}H_{10}N_4$ requires C=64·5; H=5·4; N=30·1 per cent.).

The hydrochloride was crystalline, but deliquescent.

4-p-*Tolueneazoglyoxaline*, prepared from the pure hydrochloride, crystallised from alcohol in yellow leaflets, which melted at 152° (corr.) (Found: C=63·9; H=5·5; N=31·0. $C_{10}H_{10}N_4$ requires C=64·5; H=5·4; N=30·1 per cent.).

The *hydrochloride* crystallises from dilute hydrochloric acid in fine, yellow needles forming a felted mass. The air-dried salt melts first at 76° (corr.), loses $2H_2O$ at about 117°, and melts again after darkening at 185° (corr.). It is very readily soluble in water [Found (in air-dried salt): Cl = 13·8; H_2O = 13·5. $C_{10}H_{10}N_4,HCl,2H_2O$ requires Cl=13·7; H_2O=13·9 per cent.].

We desire to thank the Salters' Institute of Industrial Chemistry for the grant of a fellowship, which has enabled one of us (L.A.R.) to take part in the investigation.

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CLVII.—*The Sulphonation of Glyoxalines.*

By Frank Lee Pyman and Leonard Allan Ravald.

Direct sulphonation of glyoxalines has not been effected previously, but in two cases derivatives of glyoxaline-2-sulphonic acid have been prepared indirectly. Thus, Anschütz (*Annalen*, 1895, **284**, 18) obtained 4 : 5-diphenylglyoxaline-2-sulphonic acid by the oxidation of 2-thiol-4 : 5-diphenylglyoxaline, whilst salts of caffeine-8-sulphonic acid are formed by the action of hot aqueous sulphites on 8-chlorocaffeine (D.R.-P. 74045).

In view of the stability and pronounced aromatic character of glyoxaline, it seemed probable that this base, like pyrazole and pyridine, would be susceptible to direct sulphonation, and this has proved to be the case, a *glyoxalinesulphonic acid* being obtained in good yield under suitable conditions. Presumably, sulphonation takes place in the 4-position, as does nitration (Fargher and Pyman, T., 1919, **115**, 217; Fargher, this vol., p. 668), and the investigation will be continued and extended to alkylglyoxalines to elucidate this point.

EXPERIMENTAL.

Glyoxaline, in the form of its sulphate, was added to sulphuric acid or fuming sulphuric acid and the mixture heated. The diluted solution was treated with barium hydroxide and subsequently with carbon dioxide, evaporated to dryness, and extracted with chloroform. This removed the unchanged glyoxaline and left crude barium glyoxalinesulphonate.

The consequences of varying the conditions appear in the following table:

No. of experiment.	Proportion of glyoxaline (base) to fuming sulphuric acid.	Strength of fuming sulphuric acid in percentage of free sulphur trioxide.	Temperature.	Duration of heating (hours).	Yield of sulphonate. Percentage of theoretical.	Glyoxaline recovered. Per cent.
1	1 : 2	(98% H_2SO_4)	100°	3	Nil.	85
2	1 : 3	12	,,	,,	Nil.	74
3	,,	40	,,	,,	4	96
4	,,	,,	160	,,	18·5	57
5	,,	,,	,,	6	9	69
6	,,	,,	200	3	11	85
7	,,	,,	260	,,	2	46
8	,,	50—60	100	,,	20	46
9	,,	,,	160	,,	52	Trace.
10	,,	,,	,,	,,	55	26
11	1 : 4	,,	,,	,,	78	Trace.
12	,,	,,	,,	,,	70	,,
13	,,	,,	,,	,,	83	,,

The crude barium glyoxalinesulphonate crystallised almost completely on treatment with water. From the pure salt the free acid and the sodium and ammonium salts were prepared by treatment with the equivalent quantities of sulphuric acid and its salts.

Glyoxalinesulphonic acid crystallises from water in large, colourless cubes which are anhydrous. It begins to soften at 290° and is entirely molten at 307° (corr.). It is soluble in about 5 parts of cold or 2 parts of hot water, but is almost insoluble in alcohol. (Found, $C=24{\cdot}2$; $H=2{\cdot}6$; $N=18{\cdot}9$. $C_3H_4O_3N_2S$ requires $C=24{\cdot}3$; $H=2{\cdot}7$; $N=18{\cdot}9$ per cent.)

Glyoxalinesulphonic acid is strongly acid to litmus, whilst its salts are only faintly alkaline. It does not combine with strong aqueous acids. On adding sodium diazobenzene-*p*-sulphonate to glyoxalinesulphonic acid in excess of aqueous sodium carbonate, no immediate coloration is produced, but a deep red colour develops in the course of a few minutes. In the presence of sodium hydroxide the solution remains pale yellow even on keeping. An attempt to nitrate glyoxalinesulphonic acid by boiling 1·1 grams with a mixture of 1 c.c. of fuming nitric acid and 1 c.c. of sulphuric acid was unsuccessful, the glyoxalinesulphonic acid being recovered unchanged.

The *barium* salt crystallises from water in colourless octahedra, which are anhydrous, soluble in 3 parts of hot water, and little less soluble in cold water, but insoluble in alcohol. (Found: $Ba=34{\cdot}2$. $(C_3H_3O_3N_2S)_2Ba$ requires $Ba=34{\cdot}1$ per cent.)

The *sodium* salt crystallises from water in large, colourless tablets, which contain $2H_2O$. It is very readily soluble in water, but almost insoluble in alcohol. (Found, in air-dried salt: $Na=11{\cdot}2$; $H_2O=17{\cdot}7$. $C_3H_3O_3N_2SNa,2H_2O$ requires $Na=11{\cdot}2$; $H_2O=17{\cdot}5$ per cent.)

The *ammonium* salt crystallises from water in large, colourless prisms. It is very readily soluble in water, and easily so in hot moist alcohol, but almost insoluble in absolute alcohol. It loses ammonia at temperatures above 100°, leaving the free acid. The air-dried salt lost 1·5 per cent. of water in a vacuum over sulphuric acid. (Found, in salt dried in a vacuum: $N=25{\cdot}4$; loss at $120°=10{\cdot}5$. $C_3H_3O_3N_2S{\cdot}NH_4$ requires $N=25{\cdot}4$; loss of $NH_3=10{\cdot}3$ per cent.)

We desire to thank the Salters' Institute of Industrial Chemistry for the grant of a fellowship which has enabled one of us (L. A. R.) to take part in the investigation.

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