49. *Experiments in the Triazine and the Glyoxaline Series.*

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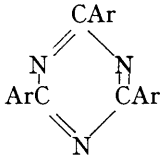
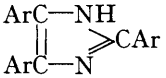
New derivatives of kyaphenine have been made by polymerising appropriately substituted benzonitriles in chlorosulphonic acid; a range of nitrokyaphenines was obtained by direct nitration and other means and these were converted into amino-kyaphenines. Reduction of the kyaphenines in acid solution afforded triarylglyoxalines, individual members being prepared also by condensing benzil or substituted benzils with aromatic aldehydes in ammonium acetate and acetic acid. New diarylglyoxalines obtained in the same way are also described. Most of the new glyoxalines exhibit chemiluminescent properties recalling those of lophine.

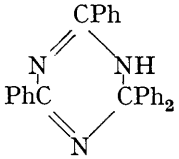
This paper describes exploratory work on the preparation of triaryltriazines (I) and related triarylglyoxalines (II). The parent members of these series are the well-known kyaphenine (I, Ar = Ph) and lophine (II, Ar = Ph).



(I.)



(II.)



(III.)

Kyaphenine has usually been made by the polymerising action of sodium (Hofmann, *Ber.*, 1868, **1**, 198) or concentrated sulphuric acid (Pinner and Klein, *Ber.*, 1878, **11**, 764) on benzonitrile. We found the best polymerising agent to be chlorosulphonic acid (D.R.-P. 549,969), which regularly afforded yields of 40% of pure kyaphenine; thionyl chloride or sulphuryl chloride was ineffective. With sodium in benzene the only isolated product was 2 : 2 : 4 : 6-tetraphenyl-1 : 2-dihydro-1 : 3 : 5-triazine (III) (cf.

Hofmann, *loc. cit.*; Lottermoser, *J. pr. Chem.*, 1896, **54**, 132). The action of boron trifluoride alone on benzonitrile gave a sublimable product, but a little kyaphenine was formed when this was heated with ammonium fluoride.

Claus and Cloetz (*J. pr. Chem.*, 1895, **51**, 399) stated that nitration of kyaphenine afforded a tri-*m*-nitro-compound, this orientation being assigned after the isolation of *m*-nitrobenzoic acid from the products of hydrolysis. In the present experiments nitration was carried out under the most diverse conditions, but always the product, whilst agreeing approximately with the description of Claus and Cloetz, was clearly not a single trinitro-compound and indeed its nitrogen content was intermediate between that required for a dinitro- and a trinitro-compound. Although we at one time considered the formation of mixed crystals and demonstrated the feasibility of this explanation of Claus and Cloetz's results by preparing molecular compounds of nitrokyaphenines prepared in other ways, nevertheless the behaviour of the direct nitration product towards reducing agents indicated that the structure had been modified in some way other than simple nitration. It is noteworthy that another compound, more probably a true tri-*m*-nitrokyaphenine, was obtained by the hazardous method of heating *m*-nitrobenzaldehyde with nitrogen sulphide (Francis and Davis, J., 1904, **85**, 261). Seeking improved methods of preparing true nitrokyaphenines, we attempted without useful result the following methods: (*a*) Polymerisation of *o*-, *m*-, or *p*-nitrobenzonitrile or mixtures of these with benzonitrile. Sodium in benzene was without action. Sulphuric acid led either to sulphonation or to the formation of small yields of kyaphenine itself. *m*- or *p*-Nitrobenzonitrile together with benzonitrile in chlorosulphonic acid gave apparently homogeneous kyaphenine-like products, which were not identical with true mono- or di-*m*- or -*p*-nitrokyaphenine, although their composition indicated this degree of nitration. In view of the likelihood of molecular compounds being formed such experiments were abandoned. Polymerisation of nitrobenzonitriles with boron trifluoride was likewise unsuccessful. (*b*) *m*- and *p*-Nitrobenzonitriles were converted into the nitro-iminoether hydrochlorides; these could not be converted into nitrokyaphenines, although benziminoether is one source of kyaphenine (Pinner, *Ber.*, 1889, **22**, 1611). *o*-Nitrobenziminoether hydrochloride has not been described; attempts to prepare it in the way that the *m*- and the *p*-compound are obtained gave an unidentified, yellow, water-soluble compound; this was " unimolecular " but was not a hydrochloride or a hydrolysis or alcoholysis product of the nitrile. (*c*) Experiments with cyanuric chloride, aluminium chloride, and nitrobenzene, or with cyanuric chloride, sodium, and bromo- or iodo-nitrobenzene did not lead to kyaphenines (cf. Klason, *J. pr. Chem.*, 1887, **35**, 83; Krafft, *Ber.*, 1889, **22**, 1760).

A number of authentic nitrokyaphenines were at length obtained by modifying a reaction by which Eitner and Krafft (*Ber.*, 1892, **25**, 2266) synthetised kyaphenine. Ammonium chloride and aluminium chloride were heated with benzonitrile and *m*-nitrobenzoyl chloride to give m-*nitrokyaphenine*. p-*Nitrokyaphenine* was obtained similarly and by using *m*- or *p*-nitrobenzonitrile with benzoyl chloride *di*-m- and -p-*nitrokyaphenines* were prepared. The reaction failed when combinations of nitriles and acid chlorides which should have yielded *o*-nitro- or trinitro-kyaphenines were used.

The properties of the trimerides of some other nitriles were also examined. *p*-Toluonitrile was most conveniently polymerised to the kyaphenine in chlorosulphonic acid. Tri-*p*-methylkyaphenine and the calculated amount of potassium nitrate in sulphuric acid afforded a *mono*-m-*nitrotri*-p-*methylkyaphenine*, but further nitration always yielded a *trinitro*-compound. The nitro-groups entered the *m*-positions, as this trinitro-compound was also produced by the polymerisation of 2-nitro-4-cyanotoluene in chlorosulphonic acid (cf. the inertness of nitrobenzonitriles). *m*-Toluonitrile and, less readily, *o*-toluonitrile as well as *p*-chlorobenzonitrile were polymerised in chlorosulphonic acid. Only two nitro-groups could be introduced into tri-*p*-chlorokyaphenine even by prolonged nitration.

When kyaphenine is reduced by acid reagents, one nitrogen atom is eliminated from the triazine ring with formation of the glyoxaline lophine (II) (Radziszewski, *Ber.*, 1882, **15**, 1493; Scholl and Nörr, *ibid.*, 1900, **33**, 1054). The preparation of representative *amino-kyaphenines* was, however, achieved by reducing the nitrokyaphenines already prepared with phenylhydrazine, and the same reduction was also effected by sodium hyposulphite.

All the amino-compounds so obtained were sparingly soluble aromatic bases which could be diazotised in pyridine solution.

The above-mentioned conversion of the triazine into the glyoxaline ring system by acid reduction seems to be general. Tri-*p*-methylkyaphenine was converted into tri-*p*-methyllophine by zinc and acetic acid (Radziszewski, *loc. cit.*) and a well-characterised *tri*-p-*chlorolophine* was obtained similarly. Reduction of available nitrokyaphenines with zinc and acetic acid, however, afforded obvious mixtures of bases, probably isomeric aminolophines. The problem of preparing individual aminolophines was then approached by first obtaining nitrolophines of known orientation.

Lophine itself is best obtained by interaction of benzil, benzaldehyde, and ammonia or of reactants which are the equivalent of these. This method has recently been improved by working with ammonium acetate in acetic acid solution (Davidson, Weiss, and Jelling, *J. Org. Chem.*, 1937, **2**, 326). These conditions were found to be excellent for preparing a wide range of substituted glyoxalines. Benzil was, for example, replaced by *p*-nitrobenzil or phenanthraquinone with formation of glyoxalines in practically theoretical yield, though it could not be replaced by diacetyl or β-naphthaquinone. On the other hand, benzil was condensed with acetaldehyde, propaldehyde, *iso*butaldehyde, salicylaldehyde, and anisaldehyde under these conditions to give excellent yields of glyoxalines; acraldehyde, crotonaldehyde, β-methylacraldehyde, and cinnamaldehyde failed to give glyoxalines. By this reaction, combination of benzil or nitrobenzil with nitrobenzaldehydes afforded a range of *nitrolophines*. They were high-melting solids, sometimes isolated in two physical modifications; they dissolved easily in caustic alkali with production of deep red colours. They were reduced by phenylhydrazine to give good yields of *aminolophines*. Here there is no risk of ring modification and the same compounds were obtained by reduction with zinc and acetic acid. They were also high-melting diazotisable bases.

It has long been known that lophine is oxidised (*e.g.*, by sodium hypochlorite and hydrogen peroxide) with production of light. Many of the glyoxalines here described exhibited similar chemiluminescent properties, although considerable variations in colour and intensity were observed. Under the conditions recommended by Cottman, Moffet, and Moffet (*Proc. Indian Acad. Sci.*, 1938, **47**, 124) the intensity was always such that a dark room was necessary for its observation. Of those examined, the chemiluminescence of tri-*p*-chlorolophine was brightest, though it was yellower and of shorter duration than that of lophine itself. 4 : 5-*Diphenyl*-2-p-*methoxyphenyl*-, -2-methyl-, -2-*ethyl*-, and -2-iso-*propyl-glyoxalines* also showed luminescence, the first yellow, the others greenish-yellow. The chemiluminescence of tri-*p*-methyl-lophine was particularly persistent. *m*-Nitrolophine was the only compound of this range which exhibited luminescence and was the only nitrolophine not readily soluble in caustic alkali. Neither of the phenanthriminazoles showed any chemiluminescence.

Experimental.

Kyaphenines.—The following method (cf. F.P. 705,407) was satisfactory. Benzonitrile (25 g.) was slowly added to chlorosulphonic acid (50 c.c.) at 0° and the viscous solution was poured on ice after standing overnight; kyaphenine, so precipitated, was recrystallised from toluene, forming small white needles (17 g.), m. p. 232°. Tri-*m*- and -*p*-methylkyaphenines were obtained in the same way. *o*-Toluonitrile (5 g.) was kept with chlorosulphonic acid (10 c.c.) at 0° for 48 hours; the solid (0·5 g.) obtained by pouring the solution on ice was sublimed at 190°/0·002 mm., and the *tri*-o-*methylkyaphenine* recrystallised from acetic acid, forming stout white rods, m. p. 110° (Found: N, 12·1. $C_{24}H_{21}N_3$ requires N, 11·9%). The crude solid (4 g.) obtained from *p*-chlorobenzonitrile (5 g.) in chlorosulphonic acid (10 c.c.) as in earlier experiments was washed with alcohol and crystallised from decalin, tri-*p*-chlorokyaphenine separating in small white needles, m. p. 335° (cf. Davis, J., 1905, **87**, 1834) (Found: N, 10·4. Calc. for $C_{21}H_{12}N_3Cl_3$: N, 10·2%).

Nitrokyaphenines.—Benzonitrile (6 g.), *m*-nitrobenzoyl chloride (4 g.), ammonium chloride (5 g.), and aluminium chloride (4·5 g.) were intimately mixed and heated overnight at 140—150°. The melt was stirred with ice and concentrated hydrochloric acid, and the precipitate collected, washed with dilute acid, and crystallised from acetic acid; m-*nitrokyaphenine* separated in small white needles (2·5 g.), m. p. 206° (Found: N, 15·9. $C_{21}H_{14}O_2N_4$ requires N, 15·8%).

p-*Nitrokyaphenine* was obtained in the same way and in similar yield by using *p*- instead of *m*-nitrobenzoyl chloride; it crystallised from acetic acid in pale yellow needles, m. p. 218° (Found: N, 15·8%). *m*-Nitrobenzonitrile (6 g.), benzoyl chloride (4 g.), ammonium chloride (5 g.), and aluminium chloride (4·5 g.), treated in the same manner, yielded *di*-m-*nitrokyaphenine*, which separated from nitrobenzene as a white crystalline powder (5·5 g.), m. p. 253° (Found: N, 17·6. $C_{21}H_{13}O_4N_5$ requires N, 17·5%). *Di*-p-*nitrokyaphenine* was obtained similarly from *p*-nitrobenzonitrile; unchanged nitrile in the crude product was sublimed at 150°/0·002 mm., and the residue crystallised from nitrobenzene, forming small pale yellow plates, m. p. 297° (Found: N, 17·5). *p*-Nitrobenzonitrile and *p*-nitrobenzoyl chloride, treated in the same manner, afforded no kyaphenine but only a ketone (*dinitrocyanobenzophenone*) crystallising from acetic acid in yellow plates, m. p. 218° (Found: N, 14·6. $C_{14}H_7O_5N_3$ requires N, 14·1%). Tri-*p*-methylkyaphenine (1 g.), dissolved in concentrated sulphuric acid (5 c.c.), was treated with powdered potassium nitrate (0·9 g.). After standing overnight, the solution was poured on ice; m-*nitrotri*-p-*methylkyaphenine* was collected and recrystallised from decalin, forming a white powder (0·9 g.), m. p. 239° (Found: N, 14·9. $C_{24}H_{20}O_2N_4$ requires N, 14·5%). 2-Nitro-4-cyanotoluene (Banse, *Ber.*, 1894, **27**, 2161) was polymerised in chlorosulphonic acid in the usual manner; the product, *tri*-m-*nitrotri*-p-*methylkyaphenine*, separated from nitrobenzene as a white granular powder, m. p. 305—307° (Found: N, 17·1. $C_{24}H_{18}O_6N_6$ requires N, 17·3%). The same product was obtained by nitrating tri-*p*-methylkyaphenine with fuming nitric acid or with more than 1 equiv. of potassium nitrate in sulphuric acid. Tri-*p*-chlorokyaphenine (1·7 g.) was warmed with fuming nitric acid (5 c.c.); a vigorous reaction set in and a white solid was precipitated. The *dinitrotri*-p-*chlorokyaphenine* had m. p. 348° after crystallising from nitrobenzene (Found: N, 13·9. $C_{21}H_{10}O_4N_5Cl_3$ requires N, 13·9%).

Aminokyaphenines.—*m*-Nitrokyaphenine (1 g.) was heated with phenylhydrazine (1 c.c.) for 3 hours at 150°. The solid residue was washed with ether and dried (0·8 g.). m-*Aminokyaphenine* crystallised from decalin in small needles, m. p. 214° (Found: N, 17·3. $C_{21}H_{16}N_4$ requires N, 17·3%). Similarly *p*-nitrokyaphenine (0·5 g.) afforded p-*aminokyaphenine* (0·35 g.), which crystallised from decalin in white needles, m. p. 273° (decomp.) (Found: N, 17·4%). This compound, when warmed with acetic anhydride and a few drops of concentrated sulphuric acid gave p-*acetamidokyaphenine*, which crystallised from decalin in white needles, m. p. 315° (Found: N, 15·3. $C_{23}H_{18}ON_4$ requires N, 15·3%). Mono-*m*-nitrotri-*p*-methylkyaphenine (1 g.) similarly yielded m-*aminotri*-p-*methylkyaphenine* (0·55 g.) as a yellow powder crystallising from decalin, m. p. 231° (Found: N, 15·4. $C_{24}H_{22}N_4$ requires N, 15·3%). Tri-*m*-nitrotri-*p*-methylkyaphenine (0·7 g.) was heated with phenylhydrazine (0·5 c.c., *i.e.*, sufficient to reduce one amino-group) as in previous examples; *di*-m-*nitrotri*-m-*amino*-p-*methylkyaphenine* (0·4 g.), so obtained and crystallised from decalin, had m. p. 261° (Found: N, 18·7. $C_{24}H_{20}O_4N_6$ requires N, 18·5%). Attempts to reduce the remaining nitro-groups by this means were unsuccessful.

Lophines.—In preparing lophine itself it was found necessary to work in more dilute solution than was suggested by Radziszewski (*Ber.*, 1882, **15**, 1493). A solution of benzil (2·5 g.) and benzaldehyde (1·2 c.c.) in alcohol (75 c.c.) was saturated with gaseous ammonia for 2 hours. Lophine, m. p. 273°, separated on evaporation of the solution to 30 c.c. When benzil (15 g.), benzaldehyde (7·5 g.), and alcohol (50 c.c.) were treated with ammonia, an unidentified compound was obtained; it separated from nitrobenzene in white plates, m. p. 268°, mixed m. p. with lophine, 225—230° (Found: N, 14·2%).

Tri-*p*-chlorokyaphenine (1·5 g.) in boiling acetic acid (50 c.c.) was treated slowly with zinc dust (5 g.). After refluxing for 20 mins., the solution was filtered and evaporated in a vacuum. The residue was dissolved in alcohol, and *tri*-p-*chlorolophine* precipitated with a little water and crystallised from alcohol or decalin, forming small white needles, m. p. 268° (Found: N, 6·5. $C_{21}H_{13}N_2Cl_3$ requires N, 7·0%).

The following is typical of preparations of other glyoxalines (cf. Davidson, Weiss, and Jelling, *loc. cit.*). Benzil (3 g.), propaldehyde (0·9 g.), and ammonium acetate (15 g.) in glacial acetic acid (75 c.c.) were refluxed for 1 hour, and the solution then poured into water. The pale yellow 4 : 5-*diphenyl*-2-*ethylglyoxaline* (3·0 g.) crystallised from alcohol in pale yellow needles, m. p. 229° (Found: N, 10·9. $C_{17}H_{16}N_2$ requires N, 11·3%). The following were similarly obtained in excellent yield: 4 : 5-*diphenyl*-2-iso*propylglyoxaline* (from benzil and *iso*butaldehyde), long, pale yellow needles from alcohol, m. p. 248° (Found: N, 10·9. $C_{18}H_{18}N_2$ requires N, 10·7%); 2-o-*hydroxyphenyl*-4 : 5-*diphenylglyoxaline* (from benzil and salicylaldehyde), yellow needles from decalin, m. p. 209° (Found: N, 9·0. $C_{21}H_{16}ON_2$ requires N, 9·0%); 2-p-*methoxyphenyl*-4 : 5-*diphenylglyoxaline* (from benzil and anisaldehyde), yellow needles from alcohol or decalin, m. p. 229° (Found: N, 8·9. $C_{22}H_{18}ON_2$ requires N, 8·6%); 2-*phenyl*-4 : 5 : 9′ : 10′-

phenanthriminazole (from phenanthraquinone and benzaldehyde), white plates from aqueous pyridine (1 : 1), m. p. 314° (Found : N, 9·8. $C_{21}H_{14}N_2$ requires N, 9·5%); 2-o-*nitrophenyl*-4 : 5 : 9′ : 10′-*phenanthriminazole* (from phenanthraquinone and *o*-nitrobenzaldehyde), pale yellow needles from alcohol, m. p. 267° (Found : N, 12·4. $C_{21}H_{13}O_2N_3$ requires N, 12·1%).

Nitrolophines.—The following were obtained by the general method described above. The glyoxalines usually separated in almost quantitative yield from the boiling reaction medium : 2-o-*Nitrophenyl*-4 : 5-*diphenylglyoxaline* (from benzil and *o*-nitrobenzaldehyde), small yellow needles from alcohol, m. p. 230° (Found : N, 11·8. $C_{21}H_{15}O_2N_3$ requires N, 12·1%); 2-m-*nitrophenyl*-4 : 5-*diphenylglyoxaline* (from benzil and *m*-nitrobenzaldehyde), yellow powder from nitrobenzene or yellow needles from aqueous pyridine, m. p. 309° (Found : N, 11·6%); 2-p-*nitrophenyl*-4 : 5-*diphenylglyoxaline* (from benzil and *p*-nitrobenzaldehyde), yellow needles from aqueous alcohol, m. p. 240° (Found : N, 12·3%); 4-p-*nitrophenyl*-2 : 5-*diphenylglyoxaline* (from *p*-nitrobenzil and benzaldehyde), yellow powder from decalin, m. p. 229° (Found : N, 12·1%); 2-o-*hydroxyphenyl*-4-p-*nitrophenyl*-5-*phenylglyoxaline* (from *p*-nitrobenzil and salicylaldehyde), orange powder from decalin, m. p. 217° (Found : N, 11·6. $C_{21}H_{15}O_3N_3$ requires N, 11·7%); 2-m-*nitrophenyl*-4-p-*nitrophenyl*-5-*phenylglyoxaline* (from *p*-nitrobenzil and *m*-nitrobenzaldehyde); this crystallised from decalin sometimes in small brown plates, m. p. 226°, sometimes as a yellow powder, m. p. 256°, the conditions deciding which form should separate remaining obscure; the lower-melting form passed into the higher on heating just above its m. p. (Found : N, 14·6. $C_{21}H_{14}O_4N_4$ requires N, 14·5%).

Aminolophines.—2-*o*-Nitrophenyl-4 : 5-diphenylglyoxaline (2 g.) was heated with phenylhydrazine (2 c.c.) at 150—160° for 2 hours. The product, 2-o-*aminophenyl*-4 : 5-*diphenylglyoxaline* (1·1 g.), crystallised from aqueous alcohol in small, pale yellow needles, m. p. 196° (Found : N, 13·4. $C_{21}H_{17}N_3$ requires N, 13·4%). The following were similarly obtained : 2-m-*Aminophenyl*-4 : 5-*diphenylglyoxaline*, yellow needles, m. p. 283° (decomp.) from nitrobenzene–decalin (1 : 1) (Found : N, 13·2%); 4-p-*aminophenyl*-2 : 5-*diphenylglyoxaline*, crystallising from decalin, m. p. 245° (decomp.) (Found : N, 13·2%). The same compounds were obtained by suspending the appropriate nitro-compounds in hot acetic acid and reducing them with zinc dust. The products were isolated by evaporation of the filtered solution to dryness, solution of the residue in hot alcohol, and precipitation with water.

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