

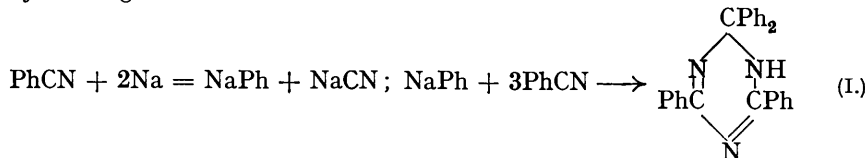
62. *The Action of Organo-alkali Compounds on Benzonitrile.*

By R. M. ANKER and A. H. COOK.

The reaction between benzonitrile and a number of alkali alkyls, aryls, and aralkyls in ether and other inert solvents at room temperature has been examined. With a sufficiency of nitrile the products are either triphenylalkyldihydrotriazines or polyphenylpyrazolines. Products of the first type which contain a primary alkyl group liberate ammonia on heating to comparatively low temperatures. The products of this novel decomposition are 2 : 4 : 6-triphenylpyrimidines, rational syntheses of which have been effected. The production of these pyrimidines establishes the structure of the parent compounds as 1 : 3 : 5-triazines. The mechanism of these reactions is

discussed and reasons are advanced for the formation sometimes of pyrazolines, sometimes of dihydrotriazines.

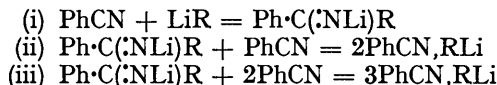
In a recent paper (Cook and Jones, this vol., p. 278) it was noted that the action of sodium on benzonitrile in hot benzene led to the formation of sodium cyanide and good yields of 2 : 2 : 4 : 6-tetraphenyl-1 : 2-dihydro-1 : 3 : 5-triazine (I). The only feasible mechanism for the formation of (I) involves the intermediate formation of phenylsodium, which then exerts a polymerising and additive action on more benzonitrile :



If this were the mechanism, the additive and polymerising stage would be expected to take place at lower temperatures and only the first stage should necessitate a raised temperature. Thus, by working with preformed alkali alkyls, aryls, and aralkyls, further representatives of a group of heterocyclic compounds hitherto largely unexplored should become available. This paper describes the action of methyl-, ethyl-, propyl-, isopropyl-, butyl-, phenyl, and benzyl-lithium, and sodiodiphenylmethane on benzonitrile.

It being postulated that the action of alkali compounds would simulate that of other organo-metallic compounds, the products of these reactions might well have been kyaphenine—the tripolymeride of benzonitrile—or ketones resulting from intermediate imines. Diethylzinc (Frankland and Evans, J., 1880, **37**, 563) and sodiophenylcyclohexylmethane (Neunhoeffler and Nerdel, *Annalen*, 1936, **526**, 47) lead to kyaphenine and many examples of the formation of ketimines from Grignard reagents are known. We showed that in boiling inert solvents the action of Grignard reagents also is often a simple polymerising one leading to kyaphenine. A number of irregular results such as the formation of pyridines and pyrazolines (Ectors, *Bull. Acad. roy. Belg.*, 1923, **9**, 501) have been reported and bases of unknown nature (see, for example, Frankland, *loc. cit.*) have been obtained. With primary and secondary nitriles these irregularities become very numerous and difficult to formulate; they undoubtedly arise from participation of the hydrogen atoms attached to the carbon atom adjacent to the nitrile group and for this reason we restricted ourselves to benzonitrile.

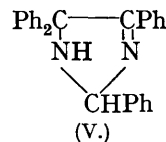
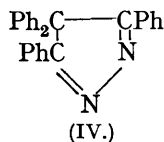
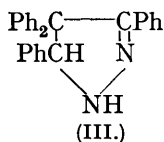
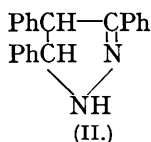
At room temperature in ether or benzene, only sodiotriphenylmethane of the alkali compounds examined exerted a simple polymerising action on benzonitrile; the reaction with metallic lithium was also mere polymerisation. In only one instance, the interaction of phenyl-lithium and benzonitrile, was any ketonic product obtained and even here the yield of ketone was very small. With these minor exceptions all the other reactions may be formulated as the formation of ketimines with subsequent addition of one or two more molecules of nitrile :



Bergmann (J., 1936, 412) treated benzonitrile with sodiodiphenylmethane and obtained the ketone $\text{CHPh}_2\cdot\text{COPh}$. We also have prepared this ketone indirectly, but our primary product of this interaction, a product which could be isolated in theoretical yield, was quite different (see below); it was obtained when the alkali compound was added to the nitrile even in equimolecular proportion.

The products containing two molecules of nitrile, that is, one molecule in addition to that which primarily forms ketimine, presented little difficulty. Such were obtained from benzyl-lithium and from sodiodiphenylmethane. The former was identical with the product of the action of benzylmagnesium chloride on benzonitrile which Ectors (*loc. cit.*) showed to be 3 : 4 : 5-triphenylpyrazoline (II). Its behaviour was closely paralleled by that of the product from sodiodiphenylmethane. This was likewise basic,

very stable towards hot acids, readily brominated in cold chloroform, and its ultra-violet absorption spectrum was practically identical with that of (II); lastly, it was oxidised



by chromic acid to a compound containing two hydrogen atoms fewer than the parent. It was therefore formulated analogously as 3 : 4 : 4 : 5-tetraphenylpyrazoline (III) and its oxidation product as the corresponding pyrazole (IV). Clearly its stability towards hydrolysing agents precluded all but cyclic structures; the only alternative, tetraphenyldihydroglyoxaline (V), which would also afford a cyclic oxidation product (tetraphenylglyoxaline), was rendered highly improbable by the product of ring-fission. The adduct was quite resistant towards acid and alkaline reagents, but when it was subjected to acetylating treatment a yellow intermediate was obtained; by boiling this with water, the colour disappeared and a non-nitrogenous ketone was obtained identical with that prepared by Bergmann (*loc. cit.*). The fission of dihydroglyoxalines on attempted acylation is not unknown (see, for example, Japp and Moir, J., 1900, **77**, 634), but the product of such fission is always an acylated base.

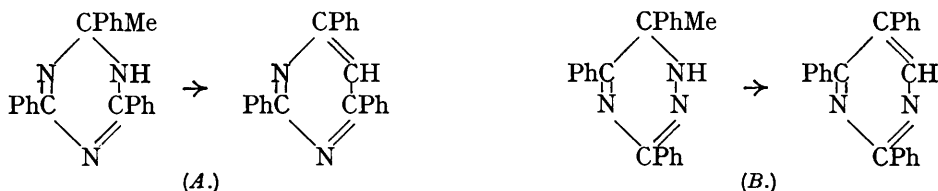
We attempted to synthesise these pyrazolines by adding diphenyldiazomethane to stilbene and to triphenylethylene in inert solvents. Unfortunately the diazo-compound failed to add to the olefin on gentle warming or irradiation in a mixture of benzene and light petroleum; this fact need occasion little surprise, however, when it is recalled that in such additions less heavily substituted olefins are usually more reactive. It was remarkable, therefore, that diphenyldiazomethane added quite readily to stilbene to give 3 : 3 : 4 : 5-tetraphenylpyrazoline isomeric with the compound obtained from sodiodiphenylmethane. It showed the same characteristic of giving yellow solutions, particularly when hot, although the solid compounds were colourless.

Methyl-, ethyl-, propyl-, isopropyl-, butyl-, and phenyl-lithium with benzonitrile all gave products of the empirical form $3\text{PhCN}, \text{RH}$; with the exception of a little benzophenone from phenyl-lithium, these were the only compounds found. The product from phenyl-lithium was identical with (I). If the course of the reaction with other alkyl-lithiums were similar, the products would again be dihydrotriazines (VI, $\text{R} = \text{Me}, \text{Et}, \text{etc.}$). This constitution was supported by the facts that the compounds were all similar strong bases forming crystalline salts; the methyl-lithium product was converted into a *mono-p-toluenesulphonyl* derivative, which was insoluble in caustic alkali as the derivative of a secondary base should be; on treatment with nitrous fumes it was converted into a product with the properties of an *N-nitroso*-compound; the absorption spectra of all these products were strikingly similar among themselves, but differed markedly from those of the pyrazolines mentioned above;

finally, any likelihood of the products possessing acyclic constitutions was eliminated by their very great stability to permanganate, chromic acid, and hydrolysing agents. No ammonia was liberated by boiling with aqueous caustic potash and the compounds were only slowly attacked by boiling with 30% sulphuric acid, ketones being generated; the product from methyl-lithium, for example, afforded acetophenone. The only remaining alternatives are unsymmetrical dihydrotriazine structures (*e.g.*, as in scheme B below). Such constituents would, it is true, be in formal respects in accord with the products containing only two molecules of nitrile which have already been formulated as pyrazolines. Unsymmetrical dihydrotriazine structures were, however, eliminated by evidence from a quite unexpected direction.

The products from methyl-, ethyl-, *n*-propyl-, or *n*-butyl-lithium lost ammonia on heating to comparatively low temperatures (250–300°). The methyl-lithium product evolved almost exactly one molecule of ammonia and the residue, remarkably free from by-products, was a crystalline, very stable compound with the formula $\text{C}_{22}\text{H}_{16}\text{N}_2$. De-

composition of the other products was less satisfactory, but led to compounds with formulæ indicating that they were homologues of the C_{22} compound. There appears to be no well-recognised mechanism by which any of the proposed structures could lose ammonia, but if the choice between symmetrical and unsymmetrical dihydrotriazine structures be admitted, then the only possible mechanism involves extrusion of a cyclic imino-group and simultaneous inclusion of a carbon atom of the alkyl group into the ring. Scheme B shows the decomposition of one of the hypothetical alternatives to (VI) :



It was thought significant as supporting this mechanism that elimination of ammonia only took place when the substituent R was a primary group containing two free hydrogen atoms as in the scheme; an acceptable explanation is thus provided of the difference between the propyl- and the *isopropyl*-lithium product, of which only the former furnished any ammonia on heating. If, now, the methyl-lithium product had structure (VI) (R = Me), its decomposition product could only be 2 : 4 : 6-triphenylpyrimidine; if it had one of the alternative structures, the decomposition product must be either 2 : 4 : 5-triphenylpyrimidine or an *o*- or *p*-diazine. Of these possibilities, only 2 : 4 : 6-triphenylpyrimidine had been prepared and this only by a series of reactions which could not be termed rational (Asahina and Kuroda, *Ber.*, 1914, **47**, 1819). The description of these workers' product agreed with ours except that they described the compound as "considerably soluble" in alcohol and 15% hydrochloric acid, whereas our product was sparingly soluble. On repeating Asahina and Kuroda's synthesis, we obtained a product which was certainly identical in every respect with our compound from benzonitrile. To remove all doubt we also synthesised 2 : 4 : 6-triphenylpyrimidine by an independent route. 6-Hydroxy-2 : 4-diphenylpyrimidine was converted into the 6-*chloro*-compound with phosphorus oxychloride and thence into triphenylpyrimidine with phenylmagnesium bromide. Again our first-mentioned product was identified with this authentic 2 : 4 : 6-triphenylpyrimidine. The primary product from methyl-lithium, then, has structure (VI) (R = Me).

On treatment of the primary product of the interaction of methyl-lithium, *i.e.*, the lithio-compound of (VI) (R = Me), with methyl iodide, methylation took place with formation of 2 : 4 : 6-*triphenyl-1 : 2-dimethyl-1 : 2-dihydro-1 : 3 : 5-triazine*. On heating, this *N*-methyl compound lost almost exactly one molecular proportion of methylamine to leave the same 2 : 4 : 6-triphenylpyrimidine as was obtained from the unmethylated base.

If thermal decomposition of the other alkyl-lithium products proceeded similarly and their structures were similar (VI, R = Et, Pr, or Bu), then the products should be 5-methyl-, 5-ethyl-, and 5-propyl-2 : 4 : 6-triphenylpyrimidine respectively. These three were synthesised by condensing the appropriate alkyl benzoylacetate with benzamidine at room temperature, converting the resulting 6-hydroxy-2 : 4-diphenyl-5-alkylpyrimidines into the 6-*chloro*-compounds, and thence with phenylmagnesium bromide, or in the case of the propyl homologue with phenyl-lithium, into triphenylalkylpyrimidines. The three pyrimidines were identical with the products from the dihydrotriazines. The suggested elimination of ammonia is thus confirmed, since groups which are introduced into the triazines as methyl, ethyl, propyl, and butyl finally appear in the pyrimidines as hydrogen, methyl, ethyl, and propyl respectively.

The mechanism of the reactions described here calls for at least one comment. It has been shown that the products are of the general form $xPhCN,RH$, where $x = 1, 2$, or 3. When $x = 3$, a triazine ring is formed with carbon and nitrogen atoms alternating in the ring, but when $x = 2$ two nitrogen atoms take up adjacent positions. The reason

(10 c.c.). About 60 drops of halide solution initiated the reaction, which was then maintained with ether refluxing without external heating; these details differ considerably from those mentioned by Gilman (*loc. cit.*). The resulting solution was syphoned into benzonitrile (30 g.); much heat was evolved and the solution was allowed to cool. Water was added, dropwise at first, and the ethereal solution dried and evaporated. Benzonitrile was recovered by distillation in a vacuum with the heating bath not above 150°; this precaution was necessary in view of the ready loss of ammonia. The residual *dihydrotriazine* solidified on cooling; it was recrystallised from ethanol, forming large crystalline clumps which sintered at 70°. Alcohol of solvation was expelled by careful fusion; the pure compound then melted at 62°, resolidified at 80—90°, and finally melted sharply at 143° (Found: C, 81.6; H, 5.6; N, 12.5. $C_{22}H_{19}N_3$ requires C, 81.3; H, 5.8; N, 12.9%). 2.5073 G. of solvated material lost 0.3198 g. on expulsion of ethanol of solvation; the apparent mol. wt. of the unsolvated material is thus 315 (calc. for $C_{22}H_{19}N_3$, 325) and the solvate must therefore be a monoalcoholate. When a solution of the free base was shaken with dilute sulphuric acid, the *sulphate* was precipitated. It was sparingly soluble in water, ethanol, or cold acetic acid, but crystallised from hot acetic acid. It decomposed at 251° but had m. p. 264° on rapid heating (Found: N, 9.8. $C_{22}H_{19}N_3 \cdot H_2SO_4$ requires N, 9.9%). The *hydrochloride*, prepared from an ethereal solution of the free base and hydrochloric acid, was readily soluble in acetic acid and crystallised with considerable loss from acetic acid-alcohol; m. p. 248° (decomp.) (Found: Cl, 9.5. $C_{22}H_{19}N_3 \cdot HCl$ requires Cl, 9.8%). The *p-toluenesulphonyl* derivative, prepared from the free base and *p*-toluenesulphonyl chloride in pyridine and crystallised from aqueous alcohol, had m. p. 240—241° (Found: N, 8.7; *M*, cryoscopic in camphor, 460. $C_{22}H_{19}N_3O_2S$ requires N, 8.8%; *M*, 480). An alcoholic solution of the base, cooled in ice, was treated with nitrous fumes. The precipitate of *N-nitroso*-compound, crystallised from ethanol, had m. p. 205° (decomp.) (Found: N, 15.6. $C_{22}H_{18}ON_4$ requires N, 15.8%). It gave a positive Liebermann reaction.

The free dihydrotriazine (0.5095 g.) was heated to 300°; 0.0273 g. was lost and 30 c.c. of a basic gas were evolved. The gas therefore had an apparent $d = 20$ and could not have been methylamine. The residue was readily soluble in benzene, ether, or hot acetic acid, sparingly soluble in ethanol or cold acetic acid, and insoluble in water; crystallised from acetic acid, it had m. p. 184° (Found: C, 85.7; H, 5.2; N, 9.2. Calc. for $C_{22}H_{18}N_2$: C, 85.7; H, 5.2; N, 9.1%). It was identical in all respects with 2:4:6-triphenylpyrimidine synthesised by the method of Asahina and Kuroda (*loc. cit.*) and it was also synthesised independently. All attempts to condense benzamidine with dibenzoylmethane in presence or absence of caustic alkali or organic bases were unsuccessful. Benzamidine (4.1 g.) was condensed with ethyl benzoylacetate (5 g.) to yield 6-hydroxy-2:4-diphenylpyrimidine, m. p. 278° (6 g. or 90% of the theoretical) (cf. Pinner, *Ber.*, 1889, 22, 1626). The hydroxy-compound was heated with excess of phosphorus oxychloride in a sealed tube overnight at 130°. Careful addition of water precipitated 6-chloro-2:4-diphenylpyrimidine, which was recrystallised from alcohol; m. p. 108° (6.0 g.) (Found: Cl, 13.0; N, 10.4. $C_{16}H_{11}N_2Cl$ requires Cl, 13.3; N, 10.5%). It was stable towards hydrolysing agents, withstanding the action of boiling aqueous caustic alkali apparently indefinitely. The chloro-compound (4 g.) was boiled with excess of phenylmagnesium bromide in toluene solution for 2 hours. The cooled solution was treated successively with alcohol, water, and dilute hydrochloric acid. The aqueous layer was extracted with ether, and the combined ether and toluene layers washed, dried, and evaporated. The residue solidified, was washed with a little ethanol, and recrystallised from acetic acid; it had m. p. 185° (yield, 4.0 g.) and was identical with the product of Asahina and Kuroda and with the product from benzonitrile.

The solution of lithiodihydrotriazine prepared as above was treated directly with methyl iodide (10 g.), and the whole refluxed for 2 hours in an atmosphere of nitrogen. On working up in the same manner, 2:4:6-triphenyl-1:2-dimethyl-1:2-dihydro-1:3:5-triazine was obtained in needles, m. p. 156°, crystallising from ethanol (Found: N, 12.4. $C_{23}H_{21}N_3$ requires N, 12.4%). The methylated base (185 mg.) was heated in a glass bulb to 300°, and the gas evolved aspirated through a saturated solution of picric acid in ether. Methylamine picrate (108 mg. or 87% of the theoretical yield), m. p. 205°, was collected; the bulb lost 18 mg. (calc. for the loss of 1 mol. of methylamine, 17 mg.) and the residue consisted of 2:4:6-triphenylpyrimidine, m. p. 185°.

2:4:6-Triphenyl-2-ethyl-1:2-dihydro-1:3:5-triazine.—Ethyl-lithium was prepared from lithium (0.8 g.), ether (60 c.c.), and freshly distilled ethyl bromide (4 c.c.) by the same procedure as was used for methyl-lithium. When the ethereal solution was syphoned into redistilled benzonitrile (15 g.), perceptible heat was evolved. The solid *dihydrotriazine* was

obtained on working up as in the case of the methyl analogue. It crystallised as an alcoholate from ethanol; alcohol was expelled by fusion before analysis, and the material then had m. p. 155° (Found: C, 82.0; H, 6.2; N, 12.2. $C_{23}H_{21}N_3$ requires C, 81.4; H, 6.2; N, 12.4%). It was readily soluble in benzene or ether, less so in alcohol.

The free base was fused at 200—300°. Considerable quantities of benzonitrile were evolved with ammonia. The residue was moistened with methanol, and the crystalline 2:4:6-triphenyl-5-methylpyrimidine recrystallised from ethanol or acetic acid; m. p. 178°. A mixture of equimolecular parts of ethyl methylbenzoylacetate (6 g.) and benzamidine hydrochloride (4.5 g.) in the minimum quantity of alcohol required to effect solution (*ca.* 20 c.c.) was treated with a slight excess of 10% caustic soda solution and kept at room temperature for 4 days. Dilute acetic acid was then added, and 6-hydroxy-2:4-diphenyl-5-methylpyrimidine filtered off and recrystallised from acetic acid, forming needles (5 g.), m. p. 253° (Found: N, 10.7. $C_{17}H_{14}ON_2$ requires N, 10.7%). The latter was heated with excess of phosphorus oxychloride at 130° for 16 hours, and unchanged phosphorus halide decomposed with water; the insoluble 6-chloro-2:4-diphenyl-5-methylpyrimidine crystallised from ethanol in needles (5 g.), m. p. 118° (Found: N, 10.0. $C_{17}H_{13}N_2Cl$ requires N, 10.0%). The chloro-compound was boiled with a large excess of phenylmagnesium bromide in toluene for 2 hours. On working up in the usual manner, 2:4:6-triphenyl-5-methylpyrimidine, crystallising from ethanol in needles, m. p. 182°, was obtained. It was identified with the former product, mixed m. p. 181° (Found: C, 86.0; H, 5.3; N, 8.6. $C_{23}H_{18}N_2$ requires C, 85.7; H, 5.6; N, 8.7%).

2:4:6-Triphenyl-2-*n*-propyl-1:2-dihydro-1:3:5-triazine.—*n*-Propyl-lithium was prepared in the same way as previous alkyl-lithiums from lithium (0.8 g.), redistilled *n*-propyl bromide (4.6 c.c.), and ether (50 c.c.). When the solution was syphoned into redistilled benzonitrile (15 g.), much heat was evolved. The solid dihydrotriazine was worked up in the usual manner; it crystallised from ethanol as an alcoholate readily soluble in benzene or ether. After expulsion of alcohol of crystallisation by fusion the dihydrotriazine melted at 50°, resolidified at *ca.* 78°, and melted again at 116° (Found: C, 82.1; H, 6.2; N, 11.9. $C_{24}H_{23}N_3$ requires C, 81.6; H, 6.5; N, 12.0%). The sulphate was obtained as with the lower homologue and crystallised from ethanol; m. p. 222° (Found: N, 9.0. $C_{24}H_{23}N_3 \cdot H_2SO_4$ requires N, 9.1%). The free dihydrotriazine was heated at 200—300°. The residue solidified when it was moistened with methanol; 2:4:6-triphenyl-5-ethylpyrimidine, crystallised from methanol or acetic acid, had m. p. 125°. Ethyl ethylbenzoylacetate and benzamidine hydrochloride were condensed as in the preceding examples. 6-Hydroxy-2:4-diphenyl-5-ethylpyrimidine (yield, 4.5 g. from 7 g. of the keto-ester) crystallised from acetic acid in needles, m. p. 266° (Found: N, 10.3. $C_{18}H_{16}ON_2$ requires N, 10.1%). Treatment of the hydroxy-compound as before afforded 6-chloro-2:4-diphenyl-5-ethylpyrimidine, which crystallised from ethanol in needles, m. p. 122° (Found: N, 9.2. $C_{18}H_{15}N_2Cl$ requires N, 9.4%). This was treated with excess of phenylmagnesium bromide in boiling toluene for 2 hours. 2:4:6-Triphenyl-5-ethylpyrimidine so obtained, and crystallised from methanol or acetic acid, had m. p. 127°. It was identical with the product of thermal decomposition of the dihydrotriazine above (Found: C, 85.6; H, 6.0; N, 8.2. $C_{24}H_{20}N_2$ requires C, 85.6; H, 6.0; N, 8.3%).

2:4:6-Triphenyl-2-isopropyl-1:2-dihydro-1:3:5-triazine.—The Grignard reagent prepared from magnesium (2.5 g.), isopropyl bromide (12.3 g.), and ether (60 c.c.) was syphoned into a suspension of lithium (1.7 g.) in ether (10 c.c.), and the whole refluxed for 3 hours. The isopropyl-lithium preparation was syphoned into benzonitrile (32 g.) and kept overnight. On cautious addition of water the dihydrotriazine was deposited; crystallised from alcohol, it had m. p. 184° (Found: C, 81.6; H, 6.8; N, 11.9; *M*, cryoscopic in camphor, 345. $C_{24}H_{23}N_3$ requires C, 81.6; H, 6.5; N, 11.9%; *M*, 353). It evolved no ammonia on heating to moderate temperatures.

2:4:6-Triphenyl-2-*n*-butyl-1:2-dihydro-1:3:5-triazine.—Lithium (0.8 g.), freshly distilled *n*-butyl chloride (5.2 c.c.), and benzene (50 c.c.) were warmed at 40—60° for 30 mins., and the tightly stoppered flask then shaken for 24 hours at room temperature. When the contents were syphoned into redistilled benzonitrile (20 g.), the mixture assumed a red colour and much heat was evolved. The dihydrotriazine was obtained in the usual manner. It was readily soluble in benzene or ether and crystallised from ethanol as a monoalcoholate (Found: N, 10.16. $C_{25}H_{25}N_3 \cdot C_2H_5 \cdot OH$ requires N, 10.17%). After being freed from alcohol by fusion, it melted at 40—50°, resolidified at 60—70°, and finally melted sharply at 117° (Found: C, 81.5; H, 6.8; N, 11.6. $C_{25}H_{25}N_3$ requires C, 81.7; H, 6.8; N, 11.5%). The same compound was obtained by preparing *n*-butyl-lithium as in the preparation of methyl-lithium. The sulphate, crystallised from 30% methanol, had m. p. 215° (Found: N, 9.1. $C_{25}H_{25}N_3 \cdot H_2SO_4$

requires N, 9.0%). The *hydrochloride* was prepared by passing hydrogen chloride into a benzene solution of the free base and evaporating the solution to crystallisation; recrystallised from 50% ethanol, it had m. p. 256° (Found: N, 10.2. $C_{25}H_{25}N_3 \cdot HCl$ requires N, 10.4%). The hydrochloride was heated at 300—310° for 1 hour. The sublimate and residue were combined and crystallised from ethanol (charcoal). 2 : 4 : 6-Triphenyl-5-*n*-propylpyrimidine so obtained had m. p. 135°. No pyrimidine was obtained by heating the free base alone or with zinc chloride, such treatment leading only to the formation of kyaphenine.

Ethyl *n*-propylbenzoylacetate (7 g.), condensed with benzamidine hydrochloride (5 g.) as in previous examples, gave 6-*hydroxy*-2 : 4-*diphenyl*-5-*n*-propylpyrimidine (6 g.), which crystallised from acetic acid in needles, m. p. 235° (Found: N, 10.0. $C_{19}H_{18}ON_2$ requires N, 9.7%). As in earlier examples, it was converted in excellent yield into 6-*chloro*-2 : 4-*diphenyl*-5-*n*-propylpyrimidine, which formed needles from ethanol, m. p. 133° (Found: N, 9.2. $C_{19}H_{17}N_2Cl$ requires N, 9.1%). To an ethereal solution of the chloro-compound, an excess of ethereal phenyl-lithium solution was added. The excess was destroyed with water almost immediately, and the solution washed with water. The ether was removed, and the residual 2 : 4 : 6-*triphenyl*-5-*n*-propylpyrimidine crystallised from ethanol; m. p. 135° (Found: N, 7.9. $C_{26}H_{22}N_2$ requires N, 8.0%). It was identical with the product obtained from the butyldihydrotriazine above.

(a) Phenyl-lithium was prepared by dropping redistilled iodobenzene (10 g.) on lithium (0.7 g.) in ether (40 c.c.) and the solution was decanted through copper gauze into benzonitrile (15 g.). The usual procedure afforded 2 : 2 : 4 : 6-tetraphenyl-1 : 2-dihydro-1 : 3 : 5-triazine (3 g.), m. p. 192°; it was identified by direct comparison with the product of Lottemoser (*J. pr. Chem.*, 1896, **54**, 132). (b) Phenylmagnesium bromide in ether was treated with benzonitrile (10 g.; 3 mols.). After 5 minutes' boiling in ethereal solution, only benzophenone was obtained. The ether was replaced by xylene (25 c.c.), and the whole boiled for 4 hours. The cooled solution was treated with alcohol, and the precipitated kyaphenine (2.5 g.) removed. The filtrate, on standing, deposited the tetraphenyldihydrotriazine. Small yields of kyaphenine alone were obtained when methyl-, ethyl-, or propyl-magnesium iodide was used.

The Grignard reagent prepared from benzyl chloride (5.7 c.c.), magnesium (1.5 g.), and ether (30 c.c.) was decanted into a bottle containing finely cut lithium (2.5 g.), and the volume of ether made up to 250 c.c. The whole was shaken at room temperature for 11 days (the red colour was then at its maximum intensity), after which the residual lithium-magnesium alloy was allowed to settle, and the benzyl-lithium solution syphoned into benzonitrile (16 g.). The colour disappeared instantly and solid 3 : 4 : 5-triphenylpyrazoline was obtained as in previous reactions; crystallised from alcohol, it had m. p. 251° (Found: C, 86.4; H, 5.0; N, 8.9. Calc. for $C_{23}H_{16}N_2$: C, 86.2; H, 5.0; N, 8.8%). It was identical in every respect with the product of Ectors (*loc. cit.*).

3 : 4 : 4 : 5-Tetraphenylpyrazoline.—Sodiiodiphenylmethane solution, prepared by shaking "molecular" sodium (1.4 g.) with benzhydryl methyl ether (6 g.) and ether (50 c.c.) overnight, was decanted into benzonitrile (9.5 g.). Some heat was generated and shaking was continued overnight. A few drops of water precipitated the *pyrazoline* in needles (9.6 g.); crystallised from benzene-light petroleum, it had m. p. 213° (Found: C, 86.6, 86.3; H, 6.2, 6.0; N, 7.5, 7.6. $C_{27}H_{22}N_2$ requires C, 86.6; H, 5.9; N, 7.5%). It was very soluble in warm acetic acid, benzene, or toluene, less soluble in alcohol, and it dissolved in dilute mineral acids. The pyrazoline was boiled for 13—15 mins. with acetic anhydride (3.5 c.c.), and the bright yellow solution decomposed with water. The insoluble colourless oil readily solidified and was recrystallised from 50% alcohol; it was identical with the ketone $C_6H_5 \cdot CO \cdot CH(C_6H_5)_2$ obtained by Bergmann (*loc. cit.*) (Found: C, 88.0; H, 5.9. Calc. for $C_{20}H_{16}O$: C, 88.2; H, 5.9%). 3 : 4 : 4 : 5-Tetraphenylpyrazoline (1 g.) in acetic acid (10 c.c.) was treated with chromic acid (0.2 g.) in hot acetic acid (7 c.c.), and the whole boiled for 3 minutes. The solution was cooled and diluted with water, and the precipitate extracted with alcohol. The residual 3 : 4 : 4 : 5-tetraphenylpyrazole crystallised from acetic acid in highly refractive cubes, m. p. 175° (Found: C, 86.8; H, 5.7. $C_{27}H_{20}N_2$ requires C, 87.0; H, 5.4%). It gave colourless solutions, whereas the parent pyrazoline always gave yellow solutions which were deeply coloured when hot, although the solid compound was colourless.

3 : 3 : 4 : 5-Tetraphenylpyrazoline.—A solution of diphenyldiazomethane in light petroleum was treated with stilbene (1 mol.) in the minimum quantity of benzene, and the mixture irradiated before a mercury vapour lamp for 3 hours. The solution, after being evaporated until crystallisation commenced, was cooled; the deposit crystallised from alcohol to give 3 : 3 : 4 : 5-tetraphenylpyrazoline, m. p. 163° (Found: C, 86.8; H, 5.7; N, 7.4. $C_{27}H_{22}N_2$

requires C, 86.6; H, 5.9; N, 7.5%). Like its isomeride above, it gave coloured solutions, particularly when hot.

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