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

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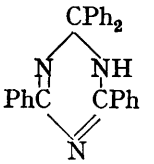
The reaction between benzonitrile and a number of alkali alkyls, aryls, and aralkyls in ether and other inert solvents at room temperature has been examined. With a sufficiency of nitrile the products are either triphenylalkyldihydrotriazines or polyphenylpyrazolines. Products of the first type which 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:

$$PhCN + 2Na = NaPh + NaCN;\ NaPh + 3PhCN \longrightarrow$$



(I.)

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-, *iso*propyl-, 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 sodiophenyl*cyclo*hexylmethane (Neunhoeffer 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.

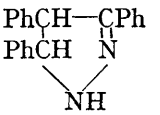
At room temperature in ether or benzene, only sodiotriphenylmethane of the alkali compounds examined exerted a simple polymerising action on benzonitrile; the reaction with metallic lithium was also mere polymerisation. In only one instance, the interaction of phenyl-lithium and benzonitrile, was any 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:

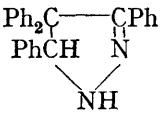
(i) $PhCN + LiR = Ph{\cdot}C(:NLi)R$
(ii) $Ph{\cdot}C(:NLi)R + PhCN = 2PhCN,RLi$
(iii) $Ph{\cdot}C(:NLi)R + 2PhCN = 3PhCN,RLi$

Bergmann (J., 1936, 412) treated benzonitrile with sodiodiphenylmethane and obtained the ketone $CHPh_2{\cdot}COPh$. 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 parallelled 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


(II.)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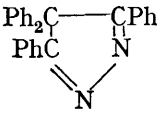
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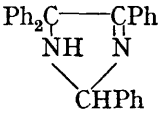
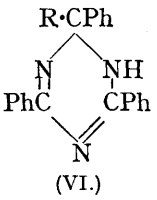

(V.)

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.

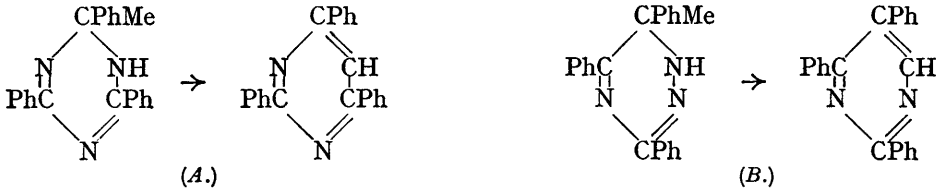
We attempted to synthesise these pyrazolines by adding diphenyldiazomethane to stilbene and to triphenylethylene in inert solvents. Unfortunately the diazo-compound failed to add to the olefin on gentle warming or irradiation in a mixture of benzene and light petroleum; this fact need occasion little 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-, *iso*propyl-, butyl-, and phenyl-lithium with benzonitrile all gave products of the empirical form 3PhCN,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 alkyllithiums were similar, the products would again be dihydrotriazines (VI, R = Me, Et, etc.). This constitution was supported by the facts that the compounds were all similar strong bases forming crystalline salts; the methyllithium 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.


(VI.)

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 $C_{22}H_{16}N_2$. 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 *iso*propyl-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.

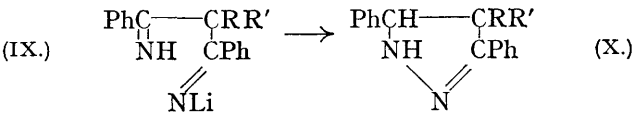
If thermal decomposition of the other alkyl-lithium products proceeded similarly and their structures were similar (VI, R = Et, Pr, or Bu), then the products should be 5-methyl-, 5-ethyl-, and 5-propyl-2 : 4 : 6-triphenylpyrimidine respectively. These three were synthesised by condensing the appropriate 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

for this difference, it is submitted, is that pyrazolines are formed only when the radical ·CHRR′ from which the alkali-metal compound is derived bears an activated hydrogen atom as in the benzyl and diphenylmethyl radicals. The first reaction stage is, as in other cases :

$$\mathrm{PhCN} + \mathrm{CHRR'Li} = \underset{\text{(VII.)}}{\mathrm{PhC(NLi)\cdot CHRR'}} \rightleftharpoons \underset{\text{(VIII.)}}{\mathrm{PhC(NH)\cdot CRR'Li}}$$

Location of the alkali-metal atom will be governed by the relative acidities of the hydrogen atoms attached to the imino-nitrogen and to the radical ·CHRR′; when this radical is of the type under discussion, it may be assumed that in further reaction with benzonitrile the effective structure will be (VIII). Succeeding stages will not lead to structures with an alternation of carbon and nitrogen atoms in the ring, for the hypothetical intermediate succeeding (VIII) must be (IX), which will cyclise to (X)



Elucidation of the constitutions of the above products was made more difficult by some unusual properties. Concordant analyses were only obtained when it became apparent that the compounds often crystallise from alcohol with one molecule of solvent which is retained with unusual tenacity. For example, the product from butyl-lithium crystallises as a monoalcoholate and loses no demonstrable proportion of alcohol even after 2 hours at 100° in a vacuum. The alcohol-free compound, and others like it, melted when recently fused at low temperatures, only to resolidify on further heating, finally melting at a comparatively high temperature. Neither this phenomenon nor the solvation appears, however, to be associated with chemical change, as it could be repeated indefinitely on the same sample.

Some less successful experiments deserve brief mention. No similar products were obtained from *p*-nitrobenzonitrile, and *o*-toluonitrile and methyl-lithium gave only an oily base. Reaction of alkyl-lithiums with phenylacetonitrile proceeded in a quite different direction, resulting in the formation of αβ-diphenylpropionitrile. Finally, in addition to the facts adduced by Linstead and Tuey (J., 1939, 1812) in connection with the formation of tetrabenztriazaporphin from methyl-lithium and phthalonitrile at a high temperature, we found in somewhat parallel experiments that a yield of 2% of pigment was obtained at the ordinary temperature in ether.

Experimental.

Note on the Preparation of Alkyl-lithiums.—For the present experiments the procedures of Gilman and collaborators (*J. Amer. Chem. Soc.*, 1932, **54**, 1957) and of Ziegler and Colonius (*Annalen*, 1930, **479**, 135) were modified. The preparations were carried out in a 3-necked nitrogen-filled flask fitted with stirrer and dropping-funnel; the third outlet led through a condenser and drying tube to a graduated bottle (1 l.) fitted with a 3-holed stopper, the other connections of which led to a nitrogen cylinder and through a syphon to a reservoir open to the air. The water level in the reservoir was arranged to be above that in the graduated bottle so as to maintain a slight excess pressure inside the apparatus. Connection was provided between the upper end of the condenser and the dropping-funnel so that the contents of the funnel flowed smoothly into the flask. On completion of the formation of the alkyl-lithium the stirrer was quickly replaced by a glass syphon fitted with a tap. The excess pressure in the apparatus then allowed the alkyl-lithium solution to be syphoned into benzonitrile.

The isolated yields of dihydrotriazines are not given, as they varied with the yield of alkyl-lithium and this depended on factors not easily controlled. As far as could be judged, the alkyl-lithium formed was converted quantitatively into dihydrotriazine.

2 : 4 : 6-*Triphenyl*-2-*methyl*-1 : 2-*dihydro*-1 : 3 : 5-*triazine*.—Methyl-lithium was prepared by adding to lithium (1·1 g.) under ether (60 c.c.), methyl iodide (4·4 c.c.) diluted with ether

(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. $C_{22}H_{19}N_3,H_2SO_4$ 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. $C_{22}H_{19}N_3$,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. $C_{29}H_{25}O_2N_3S$ 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 $C_{22}H_{16}N_2$: 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. $C_{24}H_{23}N_3,H_2SO_4$ 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-iso*propyl*-1 : 2-*dihydro*-1 : 3 : 5-*triazine*.—The Grignard reagent prepared from magnesium (2·5 g.), *iso*propyl 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 *iso*propyl-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. $C_{25}H_{25}N_3,C_2H_5{\cdot}OH$ 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. $C_{25}H_{25}N_3,H_2SO_4$

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. $C_{25}H_{25}N_3$,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. $C_{25}H_{22}N_2$ 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 Lottermoser (*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*.—Sodiodiphenylmethane 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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