324. *The Reaction of αβ-Ethynyl Ketones with Active Methyl and Methylene Compounds.*

By A. W. Johnson.

The reaction of acyl- or aroyl-acetylenes (2 mols.) and pyridines containing a 4-methyl or methylene group yields violet adducts which are represented by structures such as (III). An active " zwitterion " formed from 2 mols. of the ethynyl ketone is postulated as the intermediate in these and similar reactions. With 1 : 3 : 3-trimethylindolenine methiodide, the acyl- or aroyl-acetylenes give, after the addition of alkali, adducts formed from equimolecular quantities of the reactants, but the corresponding reaction with 2-methylbenzthiazole ethiodide resembles those with the pyridines in that 2 mols. of the ketone react with each mol. of base. The addition of ethynyl ketones to nitrogen heterocyclic compounds containing active methylene groups, *e.g.*, 1-phenyl-3-methyl-5-pyrazolone, and active methine groups, *e.g.*, 2 : 4-diphenylpyrrole and 2-methylindole, is also described.

In the course of other work on the reactions of the αβ-ethynyl ketones, $R\cdot CO\cdot C{\vdots}CH$, it was observed that when phenyl ethynyl ketone (Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, **39** was dissolved in either methylated spirits or industrial absolute alcohol, a deep violet colour rapidly developed on warming, or more slowly at room temperature. This colour was not obtained with methyl alcohol or denaturant-free alcohol. A sample of alcohol denaturant was therefore obtained and fractionated, and the colour shown to be associated with the presence of pyridine bases. Attention was then turned to the reaction of individual specially purified pyridine and quinoline homologues (0·5 c.c.) with phenyl ethynyl ketone (0·05 g.) in methyl alcohol (2 c.c.), and the following colours were observed :

Base.	Purification.	Colour.
Pyridine	Fractionation	Pale yellow
α-Picoline	Regeneration from $HgCl_2$ adduct, m. p. 153—154°	Dark reddish-brown
β-Picoline	Regeneration from oxalate,[1] m. p. 108—109°	Pale yellow
γ-Picoline	Regeneration from oxalate,[2] m. p. 139—140°	Intense reddish-violet; crystals separated on standing
4-Ethylpyridine	Fractionation [3] (synthetic)	Intense reddish-violet; crystals separated on standing
2 : 4-Lutidine	Regeneration from $HgCl_2$ adduct,[1,4] m. p. 117—119°	Intense reddish-violet; no separation of solid
2 : 6-Lutidine	Regeneration from $HgCl_2$ adduct,[1] m. p. 187—189°	Pale pink
Quinaldine	Fractionation	Pale yellow
Lepidine	Fractionation (synthetic)	Orange-red

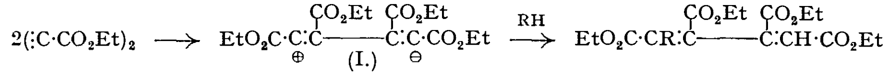
[1] Lidstone, *J.*, 1940, 241.
[2] Kolloff and Hunter, *J. Amer. Chem. Soc.*, 1941, **63**, 490.
[3] Wibaut and Arens, *Rec. Trav. chim.*, 1941, **60**, 119.
[4] Bratton and Bailey, *J. Amer. Chem. Soc.*, 1937, **59**, 177.

It was therefore apparent that the coloration observed in alcoholic solutions of phenyl ethynyl ketone was due to the presence of pyridine homologues containing active (*i.e.*, α- or γ-)

methyl or methylene groups and that violet colorations were to be particularly associated with the γ-substituted pyridines. The colour produced from the reaction of γ-picoline with phenyl ethynyl ketone proved to be sufficiently sensitive to detect 2 p.p.m. of the base in methyl alcohol. Attempts were made to apply the colour reaction to the quantitative determination of α-picoline in pyridine (γ-picoline may be readily separated from pyridine by fractionation), but the reaction proved to be less sensitive in the case of the α-isomer, and other methods for the estimation of α-picoline were found to be preferable.

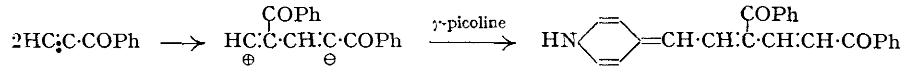
Purification and analyses of the violet *adduct* from γ-picoline and phenyl ethynyl ketone indicated a molecular formula, $C_{24}H_{19}O_2N$ (*i.e.*, $2C_9H_6O,C_6H_7N$), and this was supported by the almost quantitative yield of the adduct obtained on mixing 2 mols. of phenyl ethynyl ketone with 1 mol. of γ-picoline in a small volume of methyl alcohol. The same adduct was obtained when other alcoholic solvents, *e.g.*, 2-ethoxyethanol, were used as solvents for the reaction, but in non-polar solvents such as ether or benzene mixtures of products were formed.

It is probable that the reaction of ethynyl ketones with γ-picoline and similar compounds closely resembles those described by Diels and his co-workers (*Annalen*, 1932, **498**, 16; 1933, **505**, 103; 1934, **510**, 87; **513**, 129; 1935, **516**, 45; **519**, 140; 1936, **525**, 73; 1937, **530**, 68; 1939, **543**, 79; 1944, **556**, 38; *J. pr. Chem.*, 1940, **156**, 195; *Ber.*, 1942, **75**, 1452) in which ethyl acetylenedicarboxylate was caused to react with a variety of heterocyclic bases. It was postulated that the zwitterion (I) was an intermediate which reacted with the base as shown :

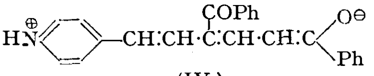


$$2(\text{:C·CO}_2\text{Et})_2 \longrightarrow \text{EtO}_2\text{C·C:}\underset{\oplus}{\overset{\text{CO}_2\text{Et}}{\text{C}}}\text{——}\overset{\text{CO}_2\text{Et}}{\text{C}}\underset{\ominus}{\text{:C·CO}_2\text{Et}}\ \text{(I.)} \xrightarrow{\text{RH}} \text{EtO}_2\text{C·CR:}\overset{\text{CO}_2\text{Et}}{\text{C}}\text{——}\overset{\text{CO}_2\text{Et}}{\text{C}}\text{:CH·CO}_2\text{Et}$$

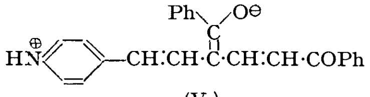
In the case of phenyl ethynyl ketone the active intermediate would be (II) by analogy, giving (III) on addition to γ-picoline :



(II.) (III.)



(IV.)

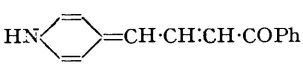


(V.)

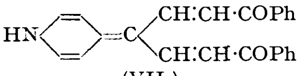
The intense violet colour of the adduct is probably due to the resonance between (III) and structures such as (IV) and (V).

A further example of phenyl ethynyl ketone reacting in the zwitterion form was encountered in the reaction with ammonium acetate in acetic acid solution, 5-benzoyl-2-phenylpyridine being obtained (cf. Bowden and Jones, *J.*, 1946, 953) together with *s*-tribenzoylbenzene.

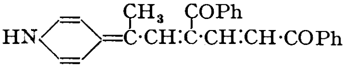
Another possible mechanism for the reaction is that the compound (VI) is the intermediate in the reaction, in which case the final adduct could be (III) or (VII). Of the two mechanisms, the former is preferred, for it will be shown later that 2 : 3 : 3-trimethylindolenine methiodide reacts with only 1 equiv. of ethynyl ketones to give adducts of the type (VI) after the addition of potassium acetate, and in no case could a second equiv. of ethynyl ketone be induced to add to the primary adduct.



(VI.)

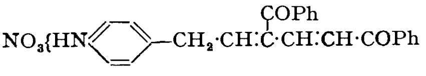


(VII.)



(VIII.)

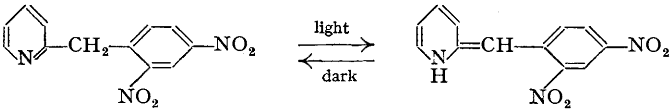
Nevertheless, structure (VII) has been eliminated on chemical grounds, for it was shown that the reaction of 4-ethylpyridine (Wibaut and Arens, *loc. cit.*) with phenyl ethynyl ketone in methanolic solution readily gave the violet adduct (VIII). The accepted structure (III) for the adduct of γ-picoline and phenyl ethynyl ketone was further supported by oxidative degradation. Oxidation with 50% nitric acid gave benzoic acid (2 mols.) and *iso*nicotinic acid (1 mol.) [*i.e.*, from the nitric acid salt (IX)], isolated as its *picrate*.



(IX.)

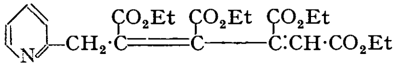
Analogues of (III) have been prepared by reaction of γ-picoline with methyl ethynyl ketone, *m*-methoxyphenyl ethynyl ketone, and *o-chlorophenyl ethynyl ketone*, severally. With *phenyl*

1-*hexynyl ketone* and γ-picoline in methanolic solution a deep blue solution was obtained but the adduct was an oil. Stable pyridine methide compounds containing no nitrogen substituents are uncommon, but Tschitchibabin, Kuindshi and Benewolenskaya (*Ber.*, 1925, **58**, 1580) have shown that the yellow compound (X) is converted into the purple isomer (XI) on irradiation. The reverse change occurs in the absence of light.

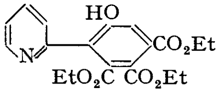


(X.) (XI.)

Diels and Pistor (*Annalen*, 1937, **530**, 87) have shown that α-picoline reacts with ethyl acetylenedicarboxylate in ethereal solution to give some of a dark red adduct formulated as (XII), which was converted into (XIII) on refluxing with methyl alcohol. No mention was made of the possibility of (XII) being in the quinonoid form.



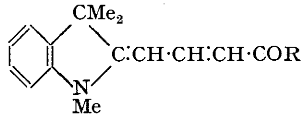
(XII.)

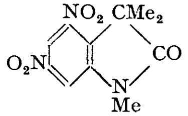


(XIII.)

The reaction of αβ-ethynyl ketones with quaternary salts containing active methyl groups has also been investigated. Phenyl ethynyl ketone with 2 : 3 : 3-trimethylindolenine methiodide, after the addition of potassium acetate to remove the elements of hydrogen iodide, gave a red crystalline compound, m. p. 158—159°, which contained no iodine, had the constitution $C_{21}H_{21}ON$, and was formulated as (XIV; R = Ph).

(XIV.)

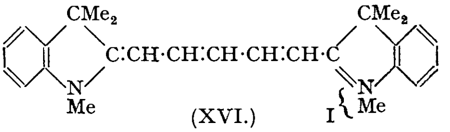




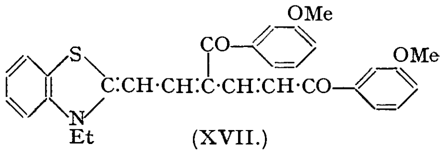
(XV.)

This formulation was supported by the almost quantitative yield of (XIV) obtained on mixing equimolecular quantities of the reactants in methyl alcohol and by the oxidation of the adduct with 50% nitric acid, whereupon 4 : 6-dinitro-1 : 3 : 3-trimethyloxindole (XV) (Beilstein, "Handbuch der Organischen Chemie", **21**, 294; Brunner, *Monatsh.*, 1896, **17**, 266) was obtained in good yield. Analogues of (XIV; R = Me and *m*-MeO·C_6H_4) have been prepared from trimethylindolenine methiodide with methyl ethynyl ketone and *m*-methoxyphenyl ethynyl ketone, respectively.

A second mol. of phenyl ethynyl ketone could not be added to (XIV) to form an adduct analogous to (III) (*e.g.*, on heating an alcoholic solution in the presence of a small amount of sodium hydroxide or piperidine or on heating in acetic anhydride) and (XIV) was always formed from the condensation of 2 : 3 : 3-trimethylindolenine methiodide and phenyl ethynyl ketone, however the ratio of the reactants was varied. The corresponding condensation of the diethylacetal of propiolic aldehyde with 2 : 3 : 3-trimethylindolenine methiodide gives rise to the indocarbocyanine dyestuff, Astrophloxine FF (XVI), and the intermediate corresponding to (XIV) has not been isolated (Bayer, G.P. 410,487).



(XVI.)

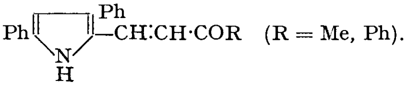


(XVII.)

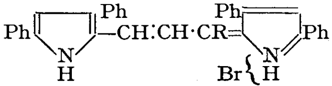
Attempts to condense (XIV; R = Me, Ph) with a second mol. of 2 : 3 : 3-trimethylindolenine methiodide have not been successful.

The reaction of 2-methylbenzthiazole ethiodide with *m*-methoxyphenyl ethynyl ketone in the presence of potassium acetate gave a moderate yield of the red *adduct* (XVII), in which 2 mols. of the ketone had reacted with each mol. of the base, but highly coloured products were not obtained from similar reactions with the ethiodides of 2-methylbenzoxazole or 2-methylbenziminazole. With quinaldine and lepidine ethiodides, dark blue adducts were obtained from the reaction with phenyl ethynyl ketone in methyl-alcoholic solution in the presence of potassium acetate, but the structure of the products has not yet been fully elucidated and will be described in a later paper.

αβ-Ethynyl ketones have also been added to active methylene and methine groups of certain nitrogen heterocyclic compounds. No basic catalyst is required to effect the addition which takes place merely on refluxing the reactants together in methyl-alcoholic solution. With 2 : 4-diphenylpyrrole (Rogers, *J.*, 1943, 590) adducts of the type (XVIII) are readily obtained, the structure of which has been proved by condensation with a further mol. of 2 : 4-diphenylpyrrole in the presence of acids to give the highly coloured salts (XIX) (Cook and Majer, *J.*, 1944, 482).



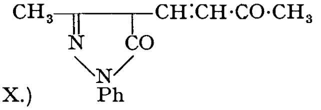
(XVIII.)

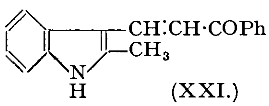


(XIX.)

The reaction of 1-phenyl-3-methyl-5-pyrazolone and methyl ethynyl ketone gave (XX), identical with the product obtained by Gaspar (B.P. 515,998) by the condensation of the pyrazolone with sodio-formylacetone. The addition of phenyl ethynyl ketone to 2-methylindole gave an *adduct* formulated as (XXI) by analogy with the additions of maleic anhydride (Diels, Alder, and Lübbert, *Annalen*, 1931, **490**, 277) and *p*-benzoquinone (Möhlau and Redlich, *Ber.*, 1911, **44**, 3605).

(XX.)





(XXI.)

EXPERIMENTAL.

(M. p.s are uncorrected, and micro-analyses were carried out by Mr. E. S. Morton.)

4-(3′ : *5′-Dibenzoylpenta-2′* : *4′-dienylidene*)-1 : *4-dihydropyridine* (III).—γ-Picoline (2·8 g.; regenerated from the oxalate) in methyl alcohol (10 c.c.) was added dropwise with stirring to a solution of phenyl ethynyl ketone (8·0 g.; Bowden, Heilbron, Jones, and Weedon, *loc. cit.*) in methyl alcohol (20 c.c.), the temperature being kept below 30°. The solution became red and then red-violet and the solid adduct was deposited almost immediately. After standing for 3 hours, the solid (10·1 g.) was separated and washed with cold methyl alcohol (20 c.c.). Rapid crystallisation from 2-ethoxyethanol gave 4-(3′ : *5′-dibenzoylpenta-2′* : *4′-dienylidene*)-1 : *4-dihydropyridine* as red-violet needles, m. p. 202—203°. Prolonged boiling of 2-ethoxyethanol solutions caused decomposition, and small quantities of the adduct may be conveniently crystallised from methyl alcohol (Found: C, 81·3; H, 5·4; N, 3·85, 4·05. $C_{24}H_{19}O_2N$ requires C, 81·6; H, 5·4; N, 4·0%). In order to obtain satisfactory carbon analyses in this series, it was necessary to mix copper oxide with the sample for combustion. Light absorption: maximum 5250 A., ε max. 6920. The adduct formed an orange solution in concentrated sulphuric acid and the red-violet methyl-alcoholic solution of the adduct was turned pink by the addition of dilute acids. The solution was unchanged in colour on addition of 2N-sodium hydroxide or 2N-ammonium hydroxide but turned yellow on addition of 10N-sodium hydroxide solution.

4-(3′ : *5′-Dibenzoyl-1′-methylpenta-2′* : *4′-dienylidene*)-1 : *4-dihydropyridine* (VIII).—4-Ethylpyridine (0·82 g.; Wibaut and Arens, *Rec. Trav. chim.*, 1941, **60**, 119) in methyl alcohol (2 c.c.) was added to phenyl ethynyl ketone (2 g.) in methyl alcohol (8 c.c.). The solution rapidly became red-violet and heat was evolved. After standing overnight, the crude solid, m. p. 217—219° (1·6 g.), was separated and crystallised from methyl alcohol (500 c.c.) to yield 4-(3′ : *5′-dibenzoyl-1′-methylpenta-2′* : *4′-dienylidene*)-1 : *4-dihydropyridine*, m. p. 232—233° (Found: C, 81·6; H, 5·7; N, 4·1. $C_{25}H_{21}O_2N$ requires C, 81·8; H, 5·7; N, 3·8%).

4-(3′ : *5′-Di-*m*-methoxybenzoylpenta-2′* : *4′-dienylidene*)-1 : *4-dihydropyridine.*—γ-Picoline (0·3 g.) in methyl alcohol (1 c.c.) was added to a solution of *m*-methoxyphenyl ethynyl ketone (1·0 g.; Johnson and Melhuish, this vol., p. 346) in methyl alcohol (5 c.c.). The mixture rapidly acquired a red-violet coloration with evolution of heat. After standing overnight, the solid (1·1 g.) was separated, washed with methyl alcohol, and crystallised from 2-ethoxyethanol, 4-(3′ : *5′-di-*m*-methoxybenzoylpenta-2′* : *4′-dienylidene*)-1 : *4-dihydropyridine* being obtained as red-violet needles, m. p. 195—196° [Found: C, 75·1; H, 5·75; OCH_3, 14·7. $C_{24}H_{17}O_2N(OCH_3)_2$ requires C, 75·5; H, 5·6; OCH_3, 15·0%].

4-(3′ : *5′-Di-*o*-chlorobenzoylpenta-2′* : *4′-dienylidene*)-1 : *4-dihydropyridine.*—γ-Picoline (0·3 g.) and *o*-chlorophenyl ethynyl ketone (1·0 g.; see below for preparation) under the conditions of the previous experiment afforded 4-(3′ : *5′-di-*o*-chlorobenzoylpenta-2′* : *4′-dienylidene*)-1 : *4-dihydropyridine* (1·0 g.), which crystallised from 2-ethoxyethanol (5 c.c.) as violet needles, m. p. 140—141° (Found: Cl, 16·9. $C_{24}H_{17}O_2NCl_2$ requires Cl, 16·8%).

4-(3′ : *5′-Diacetylpenta-2′* : *4′-dienylidene*)-1 : *4-dihydropyridine.*—γ-Picoline (0·7 g.) in methyl alcohol (1·0 c.c.) was added to a solution of methyl ethynyl ketone (1·0 g.; Bowden, Heilbron, Jones, and Weedon, *loc. cit.*) in methyl alcohol (2 c.c.) with external cooling. A vigorous reaction occurred and the solution became reddish-brown. 4-(3′ : *5′-Diacetylpenta-2′* : *4′-dienylidene*)-1 : *4-dihydropyridine* rapidly separated and after standing overnight it was collected (1·4 g.) and crystallised from methyl alcohol, forming reddish-brown needles, m. p. 202—203° (Found: C, 73·0; H, 6·75; N, 5·7. $C_{14}H_{15}O_2N$ requires C, 73·35; H, 6·55; N, 6·1%).

o-*Chlorophenylethynylcarbinol*.—Purified acetylene was rapidly passed into liquid ammonia (1000 c.c.) with stirring and cooling, and sodium (23 g.) added in small pieces at such a rate that the blue colour never persisted for more than few moments. A solution of *o*-chlorobenzaldehyde (140 g.; redistilled) in ether (150 c.c.) was added dropwise during 1½ hours, and the mixture was stirred and cooled for a further 3 hours with continued introduction of acetylene. The ammonia was allowed to evaporate overnight and ether and dilute hydrochloric acid (ice) were added to the residue. Isolation of the product in the usual manner gave o-*chlorophenylethynylcarbinol* as a pale yellow liquid (73 g.), b. p. 147—148°/26 mm.; $n_D^{24^\circ}$ 1·5669 (Found: C, 64·55; H, 4·05. C_9H_7OCl requires C, 64·85; H, 4·2%). In one experiment, *o*-chlorobenzyl alcohol, b. p. 120—125°/18 mm., m. p. 71—72°, formed by a simultaneous Cannizzaro reaction, was isolated from the lower-boiling fractions of the distillation, and it is therefore important not to add the aldehyde too quickly to the sodium acetylide solution.

o-*Chlorophenyl Ethynyl Ketone*.—To a stirred solution of *o*-chlorophenylethynylcarbinol (68 g.) in acetone (80 c.c.), a solution of chromium trioxide (38 g.) in water (120 c.c.) was slowly added in an atmosphere of nitrogen, the temperature of the solution being kept below 15°. After a further hour's stirring, the mixture was poured into water (1000 c.c.) and extracted with ether (3 × 200 c.c.). Evaporation of the ethereal solution gave a yellow solid which recrystallised from petroleum (b. p. 60—80°) to give o-*chlorophenyl ethynyl ketone* (41 g.) as pale yellow needles, m. p. 67—68° (Found: C, 65·45; H, 3·3. C_9H_5OCl requires C, 65·65; H, 3·05%). The ketone readily formed a red insoluble copper derivative and a white insoluble silver derivative.

Phenyl 1-*Hexynyl Ketone*.—A solution of chromium trioxide (9 g.) in water (28 c.c.) and concentrated sulphuric acid (7·5 c.c.) was added dropwise during 1 hour with stirring to 1-phenyl-2-hexyn-1-ol (18·2 g.; Campbell, Campbell, and McGuire, *Chem. Abs.*, 1941, **35**, 5872) in acetone (30 c.c.), the reaction temperature being kept below 15°. The mixture was further stirred for 1 hour at room temperature and then poured into water (300 c.c.), and the product isolated by means of ether. Distillation of the residue after removal of the solvent gave *phenyl* 1-*hexynyl ketone* as a pale yellow liquid (12·6 g.), b. p. 104°/1 mm.; $n_D^{22^\circ}$ 1·5451 (Found: C, 83·5; H, 7·2. $C_{13}H_{14}O$ requires C, 83·85; H, 7·5%).

Oxidation of 4-(3′ : 5′-*Dibenzoylpenta*-2′ : 4′-*dienylidene*)-1 : 4-*dihydropyridine*.—The adduct (III) (1·0 g.) was treated with nitric acid (25 c.c.; *d* 1·42) and water (25 c.c.) and refluxed for 3 hours. Nitrous fumes were evolved and the final solution was clear yellow. After standing overnight, benzoic acid (0·4 g.), m. p. 120—121° after sublimation, was deposited and was separated. The filtrate was concentrated, and on cooling, a further amount of benzoic acid (0·1 g.) was obtained, which was again separated. The filtrate was diluted with water (5 c.c.) and again concentrated, and this process repeated in order to remove the excess of nitric acid. The residue was again diluted with water (5 c.c.) and the filtered solution extracted with ether (3 × 5 c.c.). The aqueous layer was treated with excess of picric acid solution and the first-formed low-melting precipitate removed. After standing overnight, iso*nicotinic acid picrate* separated as stout yellow needles (0·25 g.), m. p. 214—215°, after crystallisation from water (Found: C, 40·65; H, 2·45; N, 15·85. $C_{12}H_8O_9N_4$ requires C, 40·6; H, 2·3; N, 15·8%). The m. p. of this derivative was not depressed on admixture with an authentic specimen, prepared from the *iso*nicotinic acid obtained by permanganate oxidation of γ-picoline (Koelsch, *J. Amer. Chem. Soc.*, 1943, **65**, 2464). A mixture of *iso*nicotinic acid picrate with *nicotinic acid picrate*, m. p. 210—211° (Found: C, 40·6; H, 2·7%), had m. p. 186—199°.

1 : 3 : 3-*Trimethyl*-2-(3′-*benzoylallylidene*)*dihydroindole* (XIV; R = Ph).—Phenyl ethynyl ketone (4·4 g.) in methyl alcohol (10 c.c.) was added to a solution of 2 : 3 : 3-trimethylindolenine methiodide (10 g.) in methyl alcohol (60 c.c.) and the mixture refluxed for 1 minute. A solution of potassium acetate (3·4 g.) in methyl alcohol (6 c.c.) was added to the yellow solution, which rapidly became red. After standing for 3 hours, the precipitated 1 : 3 : 3-*trimethyl*-2-(3′-*benzoylallylidene*)*dihydroindole* (9·0 g.; 89%) was separated, and crystallised from methyl alcohol in orange-red prisms, m. p. 158—159° (Found: C, 82·9; H, 7·2; N, 4·95. $C_{21}H_{21}ON$ requires C, 83·15; H, 6·9; N, 4·6%). Light absorption: maximum 4600 A., ε max. 45,100.

1 : 3 : 3-*Trimethyl*-2-*pent*-2′-*en*-4′-*onylidenedihydroindole* (XIV; R = Me).—Methyl ethynyl ketone (0·46 g.) in methyl alcohol (2 c.c.) was added to a solution of 2 : 3 : 3-trimethylindolenine methiodide (2 g.) in methyl alcohol (15 c.c.), and the mixture warmed slightly. A solution of potassium acetate (0·34 g.) in methyl alcohol (2 c.c.) was added, and the solution immediately became dark yellow. After standing overnight, the adduct was precipitated by cautious addition of water. 1 : 3 : 3-*Trimethyl*-2-*pent*-2′-*en*-4′-*onylidenedihydroindole* crystallised from 50% aqueous methyl alcohol in long yellow needles, m. p. 130—131° (Found: C, 79·45; H, 7·7; N, 6·05. $C_{16}H_{19}ON$ requires C, 79·65; H, 7·9; N, 5·8%). Light absorption: maximum 4150 A., ε max. 45,800.

1 : 3 : 3-*Trimethyl*-2-(3′-m-*methoxybenzoylallylidene*)*dihydroindole* (XIV; R = *m*-MeO·C_6H_4).—*m*-Methoxyphenyl ethynyl ketone (1·08 g.) in methyl alcohol (5 c.c.) was added to a solution of 2 : 3 : 3-trimethylindolenine methiodide (2 g.) in methyl alcohol (15 c.c.), and the mixture refluxed for 1 minute. A solution of potassium acetate (0·7 g.) in methyl alcohol (5 c.c.) was added, after which the solution acquired a deep red colour and the solid adduct was rapidly deposited. After standing for 3 hours, 1 : 3 : 3-*trimethyl*-2-(3′-m-*methoxybenzoylallylidene*)*dihydroindole* (2·0 g.) was separated, washed, and crystallised from methyl alcohol (300 c.c.), forming bright red plates, m. p. 182—183° (Found: C, 78·7; H, 6·5; N, 4·85. $C_{22}H_{23}O_2N$ requires C, 78·7; H, 6·5; N, 4·8%). Light absorption: maximum 4600 A., ε max. 46,300.

Oxidation of 1 : 3 : 3-*Trimethyl*-2-(3′-*benzoylallylidene*)*dihydroindole*.—The adduct (XIV; R = Ph) (1 g.) was treated with nitric acid (*d* 1·42; 25 c.c.) and water (25 c.c.) and the mixture refluxed for 3 hours. Nitrous fumes were evolved and the black tar at first produced slowly dissolved and a yellow solution was formed. After cooling, the solution was made alkaline to brilliant-yellow, any solid separated, and the solution extracted with ether (3 × 50 c.c.). Removal of the ether gave a pale brown solid (0·37 g.) which was crystallised from methyl alcohol and then from a small volume of toluene to give 4 : 6-dinitro-1 : 3 : 3-trimethyloxindole as pale yellow plates, m. p. 146—147° (Brunner, *loc. cit.*, gives m. p. 148°), alone and mixed with an authentic specimen.

3-*Ethyl*-2-(3′ : 5′-*di*-m-*methoxybenzoylpenta*-2′ : 4′-*dienylidene*)*benzthiazoline* (XVII).—*m*-Methoxyphenyl ethynyl ketone (0·52 g.) in methyl alcohol (5 c.c.) was added to a solution of 2-methylbenzthiazole ethiodide (1 g.) in methyl alcohol (5 c.c.), and the mixture warmed slightly. A solution of potassium acetate (0·32 g.) in methyl alcohol (3 c.c.) was added, whereupon the solution became deep red and a solid adduct, m. p. 150—154°, was deposited after standing overnight. The adduct (0·2 g.) was repeatedly crystallised from 2-ethoxyethanol to yield 3-*ethyl*-2-(3′ : 5′-*di*-m-*methoxybenzoylpenta*-2′ : 4′-*dienylidene*)-*benzthiazoline* as small red needles, m. p. 171—172° (Found : C, 72·5; H, 5·25; N, 2·9; S, 6·05. $C_{30}H_{27}O_4NS$ requires C, 72·45; H, 5·4; N, 2·8; S, 6·4%).

3 : 5-*Diphenyl*-2-(2′-*benzoylvinyl*)*pyrrole* (XVIII; R = Ph).—A solution of 2 : 4-diphenylpyrrole (1 g.) and phenyl ethynyl ketone (0·6 g.) in methyl alcohol (40 c.c.) was refluxed for one minute and allowed to stand overnight. 3 : 5-*Diphenyl*-2-(2′-*benzoylvinyl*)*pyrrole* (1·4 g.) crystallised in orange-red prisms, which were recrystallised from methyl alcohol. The pure adduct, m. p. 212°, dissolved in concentrated sulphuric acid to a red solution (Found : C, 85·9; H, 5·45; N, 3·85. $C_{25}H_{19}ON$ requires C, 85·9; H, 5·45; N, 4·0%).

Bis-2-(3 : 5-*diphenylpyrrole*)-α-*phenyltrimethincyanine Bromide* (XIX; R = Ph).—The foregoing compound (1·75 g.) and 2 : 4-diphenylpyrrole (1·1 g.) in acetic acid (3 c.c.) were treated with a 50% solution of hydrobromic acid in acetic acid (0·8 c.c.). An immediate deep violet coloration was produced and the mixture was warmed on the steam-bath for 40 minutes. After cooling, the adduct was separated, washed with methyl alcohol, and crystallised from chloroform to give bis-2-(3 : 5-diphenylpyrrole)-α-phenyltrimethincyanine bromide as violet prisms with a golden lustre, m. p. 245—246° (Cook and Majer, *loc. cit.*, give m. p. 245°).

3 : 5-*Diphenyl*-2-(*but*-1′-*en*-3′-*onyl*)*pyrrole* (XVIII; R = Me).—Prepared similarly to the phenyl analogue from 2 : 4-diphenylpyrrole (1 g.) and methyl ethynyl ketone (0·3 g.) in methyl alcohol (40 c.c.), and crystallised from methyl alcohol, 3 : 5-*diphenyl*-2-(*but*-1′-*en*-3′-*onyl*)*pyrrole* (1·1 g.) formed orange prisms, m. p. 207°, which dissolved in concentrated sulphuric acid to a deep orange solution (Found : C, 83·3; H, 5·85; N, 5·1. $C_{20}H_{17}ON$ requires C, 83·6; H, 5·9; N, 4·9%).

Bis-2-(3 : 5-*diphenylpyrrole*)-α-*methyltrimethincyanine Bromide* (XIX; R = Me).—The pyrrole (XVIII; R = Me) (0·3 g.) and 2 : 4-diphenylpyrrole (0·2 g.) in ethyl acetate (2 c.c.) were treated with a 50% solution of hydrobromic acid in acetic acid (0·3 c.c.), and the mixture heated on the steam-bath for one hour. The green dye was separated, and crystallised from ethyl acetate–ether, forming green plates, m. p. 224° (Cook and Majer, *loc. cit.*, give m. p. 225°).

1-*Phenyl*-3-*methyl*-4-(*but*-1′-*en*-3′-*onyl*)-5-*pyrazolone* (XX).—1-Phenyl-3-methyl-5-pyrazolone (1 g.) and methyl ethynyl ketone (0·4 g.) in methyl alcohol (10 c.c.) were refluxed for one minute, and the red solution kept at room temperature for 2 days. 1-Phenyl-3-methyl-4-(but-1′-en-3′-onyl)-5-pyrazolone was separated and crystallised from methyl alcohol, forming yellow hair-like crystals, m. p. 181° (Gaspar, *loc. cit.*, gives m. p. 177°) (Found : C, 69·7; H, 5·3. Calc. for $C_{14}H_{14}O_2N_2$: C, 69·4; H, 5·8%).

2-*Methyl*-3-(2′-*benzoylvinyl*)*indole* (XXI).—2-Methylindole (1 g.) and phenyl ethynyl ketone (1 g.) were dissolved in methyl alcohol (5 c.c.) and allowed to stand overnight. 2-*Methyl*-3-(2′-*benzoylvinyl*)-*indole* was separated, and crystallised from methyl alcohol in orange prisms, m. p. 183—184° (Found : C, 82·5; H, 5·6; N, 5·5. $C_{18}H_{15}ON$ requires C, 82·8; H, 5·75; N, 5·35%).

3-*Benzoyl*-6-*phenylpyridine and* s-*Tribenzoylbenzene*.—Phenyl ethynyl ketone (1 g.) in acetic acid (1 c.c.) was treated with a cold saturated solution of ammonium acetate (0·8 g.) in acetic acid, and the mixture kept at room temperature for 3 days. The precipitated solid was thoroughly extracted with 2N-hydrochloric acid (3 × 10 c.c.), and the acid extract basified to Clayton-yellow, whereupon crude 5-benzoyl-2-phenylpyridine was obtained. Repeated crystallisation from alcohol with carbon clarification gave the base as almost colourless plates (0·2 g.), m. p. 86—87° (Bowden and Jones, *J.*, 1946, 953, give m. p. 84—85°). The residue from the acid extract was crystallised from alcohol, and *s*-tribenzoylbenzene was obtained as colourless needles (0·3 g.), m. p. 119° (Claisen, *Annalen*, 1894, **281**, 307, gives m. p. 118—119°).

The author is indebted to Mr. J. D. Rose for his interest in this work.

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[*Received, February* 8*th*, 1947.]