# **14.** *Researches on Acetylenic Compounds. Part II.* (A) *The Addition of Amines to Ethynyl Ketones.* (B) *Auxochromic Properties and Conjugating Power of the Amino Group.*

By KENNETH BOWDEN, ERNEST A. BRAUDE, E. R. H. JONES, and B. C. L. WEEDON.

(A) The smooth addition reaction which occurs at room temperature between primary or secondary amines and ethynyl ketones, and also the interaction of hydroxymethylene derivatives of ketones with amines, lead to identical $\beta$-aminoethylenic ketones, *e.g.*, $\mathrm{R{\cdot}CO{\cdot}C{\vdots}CH \longrightarrow R{\cdot}CO{\cdot}CH{:}CH{\cdot}NHPh \longleftarrow R{\cdot}CO{\cdot}CH{:}CH{\cdot}OH}$. Evidence for the structure of these adducts, which in some cases exist in two interconvertible forms (probably geometrical isomerides), is obtained from their highly characteristic light absorption properties and also by hydrogenation to the saturated amino-ketones.

With the conjugated acetylenic ethylenic ketones (XI and XII), addition of diethylamine apparently occurs directly to the acetylenic bond and not, as might be expected, at the extremities of the conjugated system. Also, in compounds in which the ethylenic and acetylenic bonds are cross conjugated with a carbonyl group (*e.g.*, $\mathrm{CH_3{\cdot}CH{:}CH{\cdot}CO{\cdot}C{\vdots}CH}$), the addition reaction is restricted solely to the acetylenic bond, even with excess of the amine.

(B) Data for the ultra-violet light absorption of the above $\beta$-aminoethylenic ketones and, more generally, of compounds containing alkyl- and aryl-amino groups attached to the terminal carbon atom of aliphatic unsaturated systems are reported and discussed. From many examples, it is clear that alkylamino groups linked directly to an ethylenic bond produce a powerful bathochromic effect, of the same magnitude as, or even greater than, that brought about by conjugation with an additional ethylenic linkage. Thus the near ultra-violet absorption due to the $\mathrm{>C{:}C{\cdot}N<}$ grouping is similar to that of the butadiene system. This conjugating effect of the amino group is paralleled both by previously observed exaltations of molecular refractivity and by certain chemical properties somewhat akin to those of classical conjugated systems.

### (A) *The Addition of Amines to Ethynyl Ketones.*

UNTIL recently ethynyl ketones (II) have been inaccessible, but, now that they can conveniently be obtained (Part I, preceding paper) by oxidation of the corresponding carbinols with chromic acid, a systematic study of their reactions has become possible. André (*Ann. Chim.*, **1913**, **29**, 569) observed that substituted acetylenic ketones react with both primary and secondary amines, the addition of the amino group occurring in the

$$\mathrm{R{\cdot}CO{\cdot}C{\vdots}CR'} \xrightarrow{\mathrm{R_1R_2NH}} \underset{\text{(I.)}}{\mathrm{R{\cdot}CO{\cdot}CH{:}CR'{\cdot}NR_1R_2}} \qquad \underset{\text{(II.)}}{\mathrm{R{\cdot}CO{\cdot}C{\vdots}CH}} \longrightarrow \underset{\text{(III.)}}{\mathrm{R{\cdot}CO{\cdot}CH{:}CH{\cdot}NR_1R_2}}$$

β-position to the carbonyl group, giving aminoethylenic ketones of the type (I). As was to be expected it has now been found that the ethynyl ketones (II) also add amines in a similar manner, the addition of primary and secondary amines in ethereal or alcoholic solutions being exothermic. The ease with which addition takes place appears to decrease in the order : R = alkyl > propenyl > phenyl. The amino-ethylenic ketones (III) are usually formed in good yields but the crude products often consist of mixtures of geometrical isomerides; in some cases two distinct forms have been isolated, but in others only a poorer yield, probably of one of the isomeric modifications, has been obtained. Although a few examples of this addition reaction sufficed to demonstrate its nature and general character, the highly interesting light absorption properties (referred to later) of the products rendered desirable the preparation of a considerable range of these substances.

Phenyl ethynyl ketone (II; R = Ph) reacts readily with aniline in methanolic solution to give 1-anilino-3-phenylpropen-3-one (III; R = $\mathrm{R_1}$ = Ph; $\mathrm{R_2}$ = H) identical with the material obtained by Claisen and Fischer (*Ber.*, 1887, **20**, 2192) by condensation of the sodio-derivative of hydroxymethyleneacetophenone with aniline hydrochloride. These authors formulated their product as $\mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}CH{:}NPh}$, but this was rendered highly improbable by the work of von Auwers and Wunderling (*Ber.*, 1934, **67**, 644), and the present method of preparation and more especially the light absorption properties of the product are consistent only with the conjugated structure. The ethylenediamine adduct, $\mathrm{Ph{\cdot}CO{\cdot}CH{:}CH{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH{:}CH{\cdot}CO{\cdot}Ph}$ (IV), is also identical with that obtained (Benary, *Ber.*, 1930, **63**, 1576) by the hydroxymethylene-derivative method.

The reaction between methyl ethynyl ketone (II; R = Me) and aniline was unexpectedly complicated. When a cold equimolecular mixture of the two compounds in ether is allowed to stand a crystalline deposit is gradually formed. The melting point of this material is variable and values as high as 118° have been observed. On crystallisation, or merely on standing for a short time in a vacuum in the dark, the m. p. falls, a constant value of 103—104° being attained. This material is subsequently referred to as the β-form of

$$\text{(V.)}\quad \mathrm{Me{\cdot}CO{\cdot}CH{:}CH{\cdot}NHPh} \qquad\qquad \mathrm{Me{\cdot}CO{\cdot}CH_2{\cdot}CH{:}NPh}\quad \text{(Va.)}$$

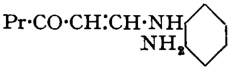
1-*anilinobut*-1-*en*-3-*one* (V) although, in fact, it is probably an equilibrium mixture of constant composition. Evaporation of the ethereal solution, after separation of the β-form, yields a red solid, m. p. *ca.* 85°. Extraction of this material with ligroin, followed by crystallisation from the same solvent or, more conveniently, sublimation of the crude material at $10^{-4}$ mm., gives the α-form of 1-*anilinobut*-1-*en*-3-*one* (V), m. p. 52—54°. Sublimation of the β-form under similar conditions gives rise to the α-isomer. This α-form is extremely unstable, being gradually converted into the β-form on standing, the melting point rising until the value of 103—104° is attained. The isomerisation is much more rapid in solution or in the molten state. Dissolution of the α-form in cold alcohol or ethyl acetate followed by rapid removal of the solvent under reduced pressure gives a product with m. p. about 90°. The isomerisation is slower in dioxan under identical conditions and from ether, light petroleum, or *cyclo*hexane the α-form is recovered unchanged. On ultraviolet irradiation of an ethereal solution for 2 minutes, however, the solvent being then removed under reduced pressure, appreciable isomerisation takes place, the product having m. p. 84°.

Thielepape (*Ber.*, 1922, **55**, 127) allowed the sodium derivative of hydroxymethyleneacetone to react with aniline hydrochloride and obtained a product, m. p. 91·5°, to which the structure (Va) was assigned. On vacuum distillation, this substance was converted into an isomer, m. p. *ca.* 61°, which, on crystallisation from aqueous alcohol, reverted to the original material (m. p. 91·5°). It seemed probable that Thielepape was dealing with impure α- and β-forms of the 1-anilinobut-1-en-3-one mentioned above, and a repetition of his work showed that this was so. Sublimation ($10^{-4}$ mm.) of the crude product obtained by his method gave the α-form, m. p. 52—54°, which was converted readily into its isomer as already indicated. Kaushal (*J. Indian Chem. Soc.*, **1943**, **20**, 53) has also obtained a compound, m. p. 247°, said to have structure (V), by treating ethoxymethyleneacetone with aniline and zinc chloride, but we consider that the material prepared by him cannot have this constitution.

The exact nature of the isomerism of the above α- and β-forms has not yet been established with certainty. The various possibilities include 3- and 5-atom, and also ring chain, prototropy as well as geometrical isomerism. The light absorption properties of the β-form are entirely consistent with the formulation (V) and this is almost certainly true of the α-form, since the same $\lambda_{\text{max.}}$ was observed in each case, although variable intensity values were recorded due, doubtless, to the isomerising influence of ultra-violet light. It is well established that geometrical isomers show maximal absorption at practically identical wave-lengths and that marked intensity differences are frequently, though not invariably, observed. The present observations together with the facts concerning the interconversions are reasonably consistent with the postulate of *cis-trans*-isomerism but a complete solution of the problem must await further study.

Addition of β-naphthylamine to methyl ethynyl ketone gives the *adduct* (III; $R = Me$, $R_1 = H$, $R_2 =$ β-naphthyl) in good yield and no obvious evidence of the existence of isomeric forms is obtained in this case. The phenomenon is again encountered, however, with the product from the reaction between propyl ethynyl ketone (II; $R = Pr^{\alpha}$) and aniline. The crude material has m. p. 77—78°; on prolonged boiling with ligroin (b. p. 40—60°) it dissolves and, when the solvent is removed, there is left an oil which freezes on cooling, giving crystals which melt below 20°. On keeping a solution of this oil in ligroin at 0° for several days, crystals of 1-*anilinohex*-1-*en*-3-*one*, (VI), m. p. 87—88°, are slowly deposited. If small quantities of the crude material are rapidly dissolved in various hot solvents and the solutions are immediately cooled, the higher melting form crystallises, but prolonged heating appears to effect conversion into the lower melting isomer.

(VI.) $\mathrm{Pr{\cdot}CO{\cdot}CH{:}CH{\cdot}NHPh}$


(VII.)

Addition reactions have also been effected between propyl ethynyl ketone and both diethylamine and piperidine, and with *o*-phenylenediamine (equimolecular quantities) the *mono-adduct* (VII) is almost exclusively produced.

Various amine adducts have been prepared from propenyl ethynyl ketone (VIII) using aniline, piperidine, diethylamine and *p*-nitroaniline; with benzidine, a di-adduct was readily obtained. In a number of these examples the yields of pure crystalline adducts were low, presumably due to the presence of stereoisomerides. With this ketone mono-addition could conceivably occur at either the ethylenic or acetylenic linkages; the light absorption of the adducts shows, however, addition at the triple bond as indicated below. This point has been conclusively proved in the case of the products from the first two amines mentioned above by hydrogenating the adducts (IX) to the saturated amino-ketones (X), which proved to be identical with materials prepared from β-chloroethyl propyl ketone. Further reaction of the adducts (IX) with amines is difficult to effect, the starting materials being recovered unchanged after 24 hours at 100°.

$$\underset{\text{(VIII.)}}{\mathrm{Me{\cdot}CH{:}CH{\cdot}CO{\cdot}C{\vdots}CH}} \xrightarrow{\mathrm{NHR_1R_2}} \underset{\text{(IX.)}}{\mathrm{Me{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}NR_1R_2}} \xrightarrow{\mathrm{H_2/Pt}}$$

$$\underset{\text{(X.)}}{\mathrm{Me{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}NR_1R_2}} \xleftarrow{\mathrm{NHR_1R_2}} \mathrm{Me{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2Cl}$$

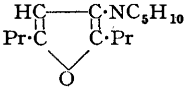
The adducts prepared with diethylamine and piperidine readily form picrates, whereas those obtained from aniline and other aromatic amines do not, and appear to have only weakly basic properties. They are soluble in mineral acids but probably undergo fission and hydration during this process since they cannot be recovered unchanged. With 2 : 4-dinitrophenylhydrazine sulphate, probably owing to its acidic nature, complex products are produced, and even with semicarbazide acetate, in the single case studied (the adduct of propyl ethynyl ketone and piperidine), the product is the bis-semicarbazone of the nitrogen free hydration product.

The addition of equimolecular amounts of diethylamine to the three conjugated ethylenic acetylenic ketones (XI and XII; $R = H$ and Me) proceeds smoothly at the ordinary temperature, the addition occurring in each case at the acetylenic linkage. It seemed possible that with (XII; $R = H$), 1 : 6-addition might lead to the same adduct (XIII) as is obtained from hex-3-en-5-yn-2-one (XI), but the two products are different, especially in their light absorption properties (see below).

$$\underset{\text{(XI.)}}{\mathrm{Me{\cdot}CO{\cdot}CH{:}CH{\cdot}C{\vdots}CH}} \xrightarrow{\mathrm{NHEt_2}} \underset{\text{(XIII.)}}{\mathrm{Me{\cdot}CO{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}NEt_2}};\quad \underset{\text{(XII.)}}{\mathrm{Me{\cdot}CO{\cdot}C{\vdots}C{\cdot}CR{:}CH_2}} \xrightarrow{\mathrm{NHEt_2}} \underset{\text{(XIV.)}}{\mathrm{Me{\cdot}CO{\cdot}CH{:}C(NEt_2){\cdot}CR{:}CH_2}}$$

In the case of the keto-alcohol (XV) addition of piperidine is accompanied by cyclisation (of the hypothetical intermediate ethylenic keto-alcohol) to the 3-*piperidino*-2 : 5-*dipropylfuran* (XVI), a reaction closely related to certain hydrations described in Part IV of this series (p. 54).

$\mathrm{Pr{\cdot}CH(OH){\cdot}C{\vdots}C{\cdot}CO{\cdot}Pr}$
(XV.)



(XVI.)

### (B) *Auxochromic Properties and Conjugating Power of the Amino Group.*

Light absorption data for the various amino-ethylenic ketones and also for certain αβ-unsaturated amines, all of the general type $\mathrm{XCH = CH{\cdot}NRR'}$, are given in the accompanying table and figure together with comparative data for the corresponding unsubstituted systems, *i.e.*, $\mathrm{XCH = CH_2}$. The introduction of an amino group at the terminal carbon atom in a conjugated system of the butadiene or methyl vinyl ketone type results in pronounced bathochromic and hyperchromic displacements of maximal absorption ($+ \Delta\lambda = 500$—1000 A; $+ \Delta\varepsilon =$ 2500—20,000). These are even considerably greater in magnitude than those displacements normally produced —and well exemplified in the literature—by substitution with additional ethylenic or other unsaturated groups. Moreover, even the conjugation of a single ethylenic bond with an amino group, *e.g.*, in (1), results in light absorption equivalent to that exhibited by classical conjugated systems such as butadiene.

The amino group has long been recognised as one of the principal auxochromes in classical colour theory, and its variochromic properties when substituted in aromatic systems are well known. Thus, introduction of an amino group into benzene or pyridine, or into the benzene nuclei of styrene, acetophenone, diphenyl, stilbene, etc., produces displacements of $\lambda_{max.}$ towards higher wavelengths and increases in $\varepsilon_{max.}$ (Pestemer, Langer, and Manchen, *Monatsh.*, 1936, **68**, 326; Pestemer and Mayer-Pitsch, *ibid.*, 1937, **70**, 104; Hertel and Lührmann, *Z. physikal. Chem.*, 1939, **44**, 261); similarly, the successive substitution of amino groups into the benzene nuclei of triphenylmethane dyestuffs results in absorption further and further towards the red region of the visible spectrum. In aliphatic systems, the auxochromic effects of the amino group have hitherto been much less clearly established, although it has recently been shown that the increase in $\lambda_{max.}$ observed in αβ-ethylenic semicarbazones as compared with the parent carbonyl compounds must be ascribed to the conjugating power of the >NH group as such, and not to an extension of the conjugated system through enolisation (Braude and Jones, *J.*, 1945, 498; Burawoy, *J.*, 1941, 20; Evans and Gillam, *J.*, 1943, 565). The substitution in *p*-benzo-

TABLE

*Light Absorption of Unsaturated Amines.*

(In alcohol except where otherwise stated.)

| Amine. | $\lambda_{max.}$, A. | $\varepsilon_{max.} \times 10^{-2}$. | Corresponding hydrocarbon or ketone. | $\lambda_{max.}$, A. | $\varepsilon_{max.} \times 10^{-2}$. | Δλ. | $\Delta(\varepsilon \times 10^{-2})$ |
|---|---|---|---|---|---|---|---|
| (1) $CHEt{=}CH\cdot\mathbf{N}C_5H_{10}$ (piperidyl) | 2280 | 100 * | $CHEt{=}CHBu^{\alpha}$ [1] | 1850 | 80 | 430 | 20 |
| (2) $CH_2{=}CH\cdot CH{=}CH\cdot\mathbf{N}Et_2$ | 2810 | 235 * | $CH_2{=}CH\cdot CH{=}CH_2$ [2] | 2170 | 210 | 640 | 25 |
| (3) $EtO\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CMe\cdot\mathbf{N}Et_2$ | 2850<br>2880 | 305 | $EtO\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CHMe$ [3] | 2000 | 200 | 880 | 105 |
| (4) $Pr\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CH\cdot\mathbf{N}Et_2$ | 2150<br>3070 | 12<br>280 | $Me\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CH_2$ [7] | 2100 | 65 | 970 | 215 |
| (5) $Pr\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CH\cdot\mathbf{N}C_5H_{10}$ (piperidyl) | 2200<br>3080 | 13<br>280 | ,, | 2100 | 65 | 980 | 215 |
| (6) $Me\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CH\cdot\mathbf{NHPh}$ | 2280<br>3380 | 110<br>275 | ,, | 2100 | 65 | 1280 | 210 |
| (7) $Pr\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CH\cdot\mathbf{NHPh}$ | 2270<br>3400 | 95<br>245 | ,, | 2100 | 65 | 1300 | 180 |
| (8) $Pr\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CH\cdot\mathbf{NHC_6H_4\cdot N}H_2$ (*o*) | 2360<br>2405<br>3480 | 115<br>115<br>155 | ,, | 2100 | 65 | 1380 | 90 |
| (9) $Me\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CH\cdot\mathbf{NHC_{10}H_7}$ (*β*) | 2290<br>2600<br>2820<br>2920<br>3500 | 355<br>115<br>135<br>160<br>315 | ,, | 2100 | 65 | 1400 | 250 |
| (10) $CHMe{=}CH\cdot\underset{\underset{O}{\|}}{C}\cdot\mathbf{N}Et_2$ | 2150<br>2420 | 110<br>65 | $MeCH{=}CH\cdot\underset{\underset{O}{\|}}{CH}$ [4] | 2170 | 155 | −20 | −45 |
| (11) $Me\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CH\cdot CH{=}CH\cdot\mathbf{N}Et_2$ | 2270<br>2420<br>3780 | 35<br>30<br>465 | $Me\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CH\cdot CH{=}CH_2$ [5] | 2630 • | 220 | 1150 | 245 |
| (12) $Me\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}\underset{\underset{\mathbf{N}Et_2}{\vert}}{C}\cdot CH{=}CH_2$ | 3080 | 185 | ,, | 2630 | 220 | 450 | −35 |
| (13) $Me\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}\underset{\underset{\mathbf{N}Et_2}{\vert}}{C}\cdot CMe{=}CH_2$ | 3100<br>3150 | 305 | $Me\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CH\cdot CHMe{=}CH_2$ | 2710 | 225 | 440 | 80 |
| (14) $CHMe{=}CH\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CH\cdot\mathbf{N}Et_2$ | 2425<br>3390 | 105<br>240 | $CHMe{=}CH\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CH_2$ [7] | 2360 | 95 | 1030 | 145 |
| (15) $CHMe{=}CH\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CH\cdot\mathbf{N}C_5H_{10}$ (piperidyl) | 2420<br>3420 | 110<br>255 | ,, | 2360 | 95 | 1060 | 160 |
| (16) $CHMe{=}CH\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CH\cdot\mathbf{NHPh}$ | 2400<br>3770 | 165<br>295 | ,, | 2360 | 95 | 1410 | 200 |
| (17) $CHMe{=}CH\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CH\cdot\mathbf{NHC_6H_4\cdot NO_2}$ (*p*) | 2290<br>2440<br>3940 | 120<br>120<br>445 | ,, | 2360 | 95 | 1580 | 350 |
| (18) $(CHMe{=}CH\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CH\cdot\mathbf{NHC_6H_4})_2$ | 2290<br>2450<br>4130 | 140<br>140<br>530 | ,, | 2360 | 95 | 1770 | 435 |
| (19) $(\mathbf{Ph}\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CH\cdot\mathbf{N}H\cdot CH_2)_2$ | 2420<br>2450<br>3450 | 220<br>335 | $\mathbf{Ph}\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CH_2$ | 2475 | 105 | 975 | 230 |
| (20) $\mathbf{Ph}\cdot\underset{\underset{O}{\|}}{C}\cdot CH{=}CH\cdot\mathbf{NHPh}$ | 2420<br>2540<br>3740 | 175<br>175<br>310 | ,, | 2475 | 105 | 1265 | 205 |

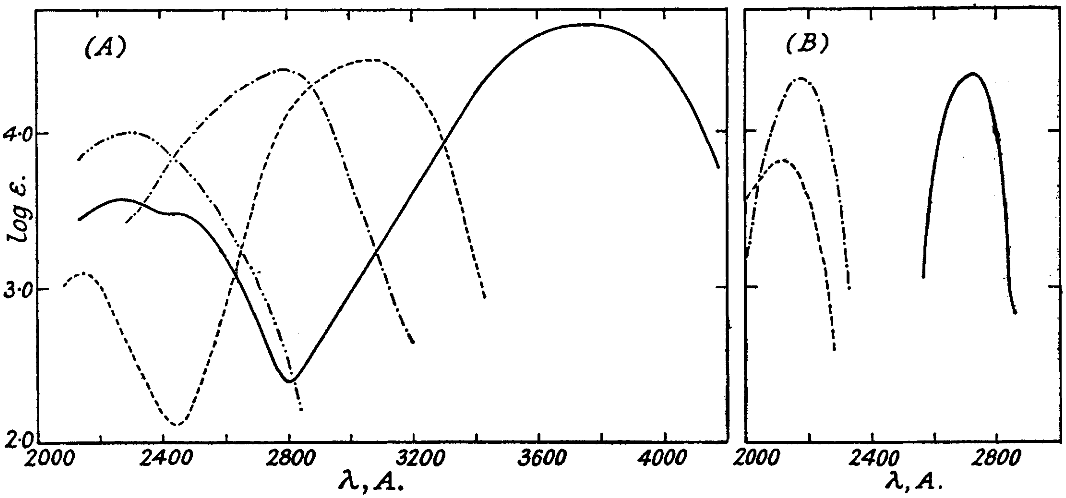
* In hexane.

[1] Platt, Rusoft, and Klevens, *J. Chem. Physics*, 1943, **11**, 535. [2] Smakula, *Angew. Chem.*, 1934, **47**, 657. [3] Grossmann, *Z. physikal. Chem.*, 1924, **109**, 305. [4] Hausser, Kuhn, Smakula, and Hoffer *Z. physikal. Chem.*, 1935, **29**, 371. [5] Calculated from data for Me·CO·(CH:CH)$_2$·Me ($\lambda_{max.}$ 2710 A.; ε 22,500; Smakula, *loc. cit.*) assuming effect of methyl group as observed with dienes (Booker, Evans and Gillam, *J.*, 1940, 1453).

[6] Assumed to be same as Me·CO·(CH:CH)$_2$·Me. [7] See Part I. (preceding paper).

quinone by amino groups results in a similar displacement of the high intensity absorption band, the latter probably originating in a chromophoric system of the aliphatic type (Braude, *J.*, 1945, 490). Again, in the 2 : 4-dinitrophenylhydrazones of αβ-unsaturated carbonyl compounds, the >NH group permits conjugation between the aliphatic and aromatic portions of the molecule (Braude and Jones, *loc. cit.*).

The present results illustrate in a more direct, simple and conclusive manner that the amino group in aliphatic systems possesses conjugating power similar to that of an ethylenic bond in many respects. This property is clearly to be ascribed to the presence of the unshared electron pair on the nitrogen atom and its capacity to provide a seat for a positive charge. Fixation of this free electron pair by quaternary salt formation completely destroys the powerful auxochromic properties. Thus (1) in 1M-hydrochloric acid solution shows only low intensity absorption above 2100 A. (the original material being recovered from the solution after the measurements (see Experimental)), and this is paralleled by the well known reversion of the ultra-violet absorption of aniline to that of benzene in strongly acid solution. Similarly, neurine bromide, containing a quaternary nitrogen atom adjacent to an ethylenic linkage, shows no high intensity absorption beyond 2100 A. (Castille and Ruppol, *Bull. Soc. Chim. biol.*, 1928, **10**, 639).



———— { *A* $Me\cdot CO\cdot CH{=}CH\cdot CH{=}CH\cdot NEt_2$
*B* $Me\cdot CO\cdot CH{=}CH\cdot CH{=}CH\cdot CH_3$ }

– – – – – – { *A* $Pr\cdot CO\cdot CH{=}CH\cdot NEt_2$
*B* $Me\cdot CO\cdot CH{=}CH_2$ }

—·—·—·— { *A* $CH_2{=}CH\cdot CH{=}CH\cdot NEt_2$
*B* $CH_2{=}CH\cdot CH{=}CH_2$ }

—··—··—·· *A* $Et\cdot CH{=}CH\cdot NC_5H_{10}$

Exaltation of molecular refractivity, which is closely related to selective absorption in the ultra-violet, is also observed with αβ-ethylenic amines. The refractivity of β-amino- and β-alkylamino-crotonic esters and of β-amino- and β-alkylamino-αβ-ethylenic ketones has been shown to correspond to the interaction of three conjugated unsaturated groups (Brühl, *Ber.*, 1907, **40**, 878, 1153; Eisenlohr, " Spektrochemie Organischer Verbindungen," Stuttgart, 1912, pp. 111, 153; von Auwers and Susemihl, *Ber.*, 1930, **63**, 1072; Glickmann and Cope, *J. Amer. Chem. Soc.*, 1945, **67**, 1017). The analogy, however, between the spectral properties of the amino group and the ethylenic bond is limited; the conjugating power of the former is not exerted in combination with a second amino group or when attached directly to a carbonyl group. Hydrazine, acetamide and urea exhibit neither high intensity light absorption above 2100 A. nor optical exaltation (Bielecki and Henri, *Compt. rend.*, 1913, **156**, 1860; Braude and Jones, *loc. cit.*; Castille and Ruppol, *loc. cit.*; Brühl, *loc. cit.*; Eisenlohr, *loc. cit.*), and both crotonamide (Bruylants, *Bull. Acad. roy. Belg.*, 1927, **130**, 767) and *N*-diethylcrotonamide (10) have light absorption properties practically identical with those of crotonaldehyde.

The resemblance between the optical properties of $-C{=}C-C{=}C-$ and $-C{=}C-N<$ systems is paralleled by some similarities in chemical properties. Decker and Klauser (*Ber.*, 1904, **37**, 523) and Decker (*ibid.*, 1905, **38**, 2893) suggested and examined the possibility that conjugation existed between ethylenic linkages and the " addition valencies " of adjacent tervalent nitrogen atoms, and Robinson (*J.*, 1916, 1038) provided convincing evidence for this hypothesis by his studies on the *C*-alkylation of certain derivatives of β-aminocrotonic acid, thus :

$$NEt_2\cdot CMe{=}CH\cdot CO_2Et + MeI \longrightarrow I[NEt_2{=}CMe\cdot CHMe\cdot CO_2Et]$$

This terminal addition to the conjugated system is reminiscent of the 1 : 4-addition undergone by diene systems. The strong positive tautomeric (electron repelling) effect of the amino group, exemplified, *inter alia*, by its *ortho-para* directing influence in aromatic substitution, is similarly related to its spectral conjugating power and, like the latter, it is inhibited if the free electron pair is immobilised through quaternary salt formation, *e.g.*, in acid solution.

The data presented in the table may now be considered in somewhat greater detail. Substitution of the piperidyl group into butene and of the diethylamino group into butadiene (1 and 2) results in displacements of $\lambda_{\max.}$ of 430 and 640 A. respectively, $\varepsilon_{\max.}$ remaining practically unaltered. In purely ethylenic systems tertiary amino groups thus have a bathochromic effect rather greater than that observed with an ethylenic double bond (*i.e.*, $+ \Delta\lambda = 300$—400 A.) (Euler, Karrer, Klussmann, and Morf, *Helv. Chim. Acta*, 1932, **15**, 502; Hausser, Kuhn, Smakula, and Hoffer, *Z. physikal. Chem.*, 1935, **29**, 371), but no hyperchromic effect is observed. Substitution of tertiary amino groups in the β-position of αβ-unsaturated carbonyl compounds gives rise to larger bathochromic and large hyperchromic shifts ($+ \Delta\lambda = 970$ A.; $+ \Delta\varepsilon = 21{,}500$), and an analogous effect is observed with αβ-unsaturated esters (3) (cf., Glickmann and Cope, *loc. cit.*). Subsidiary bands are also present in all cases. Attachment of dialkylamino groups to the terminal carbon atom of triply conjugated systems (11, 14, 15, 19) results in still larger wavelength displacements ($+ \Delta\lambda =$ *ca.* 1100 A.) than those observed on substitution in αβ-ethylenic ketones, and the bathochromic effect of the amino group, unlike that of the ethylenic bond (Hausser *et al.*, *loc. cit.*), appears to be enhanced with increasing extent of the conjugated system to which it is attached. As would be expected, however, if the amino group forms a branch of the conjugated system (" cross conjugation ") (12, 13), the bathochromic effect is much smaller ($+ \Delta\lambda =$ *ca.* 450 A.).

Arylamino groups give rise to larger variochromic effects than alkylamino groups, as well as to subsidiary bands of benzenoid origin (6, 7, 8, 16, 17, 18), and hence the amino group is clearly capable of transmitting conjugation between aliphatic and aromatic systems, as has previously been noted (Braude and Jones, *loc. cit.*). The increments in $\lambda_{\max.}$ due to NHPh groups are about 300 A. greater than those due to dialkylamino groups, so that $\Delta\lambda_{\mathrm{Ph}}$ is approximately equal to $\Delta\lambda_{\mathrm{C=C}}$ in these systems. The benzidine derivative (18) absorbs well into the visible region of the spectrum, the position of the principal maximum corresponding to the interaction of about nine conjugated ethylenic linkages, indicating some transmission of conjugation through the diphenyl group.

The comparative effects of the amino, alkylamino and dialkylamino groups, and of other substituents will be reported in a future publication.

## EXPERIMENTAL.

The preparation of the ethynyl ketones is described in the preceding paper.

### (i) *Additions to Phenyl Ethynyl Ketone.*

1-*Anilino*-3-*phenylpropen*-3-*one* (III; R = R$_1$ = Ph, R$_2$ = H).—A solution of aniline (0·7 g.) in methyl alcohol (15 c.c.) was added gradually to a solution of phenyl ethynyl ketone (1 g.) in methyl alcohol (15 c.c.), the temperature being kept below 45°. The separated solid gave, on crystallisation from methanol, 1-anilino-3-phenylpropen-3-one (1·2 g.) as lemon-yellow needles, m. p. 140—141°, undepressed on admixture with an authentic specimen made by allowing the sodium derivative of hydroxymethyleneacetophenone to react with aniline hydrochloride (Claisen and Fischer, *Ber.*, 1887, **20**, 2192).

N:N′-*Bis*-(2-*benzoylvinyl*)-*ethylenediamine* (IV).—A solution of phenyl ethynyl ketone (3 g.) in methyl alcohol (25 c.c.) was added gradually to ethylenediamine monohydrate (0·8 g.) in methanol (20 c.c.) below 40°. The separated solid when crystallised from methanol gave N:N′-bis-(2-benzoylvinyl)-ethylenediamine (2·5 g.) as pale yellow leaflets, m. p. 142°, undepressed on admixture with a specimen prepared from the sodium derivative of hydroxymethyleneacetophenone and ethylenediamine dihydrochloride (Benary, *Ber.*, 1930, **63**, 1576).

### (ii) *Additions to Methyl Ethynyl Ketone.*

1-*Anilinobut*-1-*en*-3-*one* (V).—(a) (cf., Thielepape, *Ber.*, 1922, **55**, 127). A solution of aniline hydrochloride (10·3 g.) in water (75 c.c.) was added to a stirred solution of the sodium derivative of hydroxymethyleneacetone (10 g.) in water (40 c.c.) at 5° in an atmosphere of nitrogen. Isolation of the separated oily product with ether and distillation at 80° (bath temp.)/10$^{-4}$ mm. followed by crystallisation of the resulting solid (4·8 g.) from ligroin (b. p. 40—60°) gave α-1-*anilinobut*-1-*en*-3-*one* (4·3 g.), as needles, m. p. 52—54° (Found : C, 74·65; H, 6·7. $C_{10}H_{11}ON$ requires C, 74·5; H, 6·9%).

(b) Aniline (5·5 g.) was slowly added to a cooled solution of the ethynyl ketone (4 g.) in ether (25 c.c.) and after standing for 12 hours at 20° and 2 days at 0° a yellow solid (5 g.), m. p. 108—110°, was obtained (from some experiments crude products with m. p. as high as 118° have been isolated). Recrystallisation from aqueous acetone gave β-1-*anilinobut*-1-*en*-3-*one* (4·5 g.) as pale yellow plates, m. p. 103—104·5° (Found : N, 8·85. $C_{10}H_{11}ON$ requires N, 8·7%). Evaporation of the mother liquors gave a red solid (3·4 g.; m. p. *ca.* 85°) from which, on sublimation at 80—90° (bath temp.)/10$^{-4}$ mm. the α-form (1·85 g.), m. p. 52—54°, undepressed on admixture with a specimen obtained by method (a), was obtained.

1-(β-*Naphthylamino*)-*but*-1-*en*-3-*one* (III; R = Me, R$_1$ = H, R$_2$ = β-$C_{10}H_7$).—To a solution of β-naphthylamine (21 g.) in ether (350 c.c.) methyl ethynyl ketone (10 g.) was gradually added, and after standing overnight at 20°, evaporation gave a crude product (26 g.), m. p. 104°. Chromatography from a benzene solution on alumina followed by crystallisation from aqueous alcohol gave 1-(β-*naphthylamino*)-*but*-1-*en*-3-*one* (17 g.) as leaflets, m. p. 140—141° (Found : C, 79·75; H, 6·2. $C_{14}H_{13}ON$ requires C, 79·6; H, 6·2%).

### (iii) *Additions to Propyl Ethynyl Ketone.*

1-*Anilinohex*-1-*en*-3-*one* (VI).—The addition of aniline (4·5 g.) to the ketone (4·5 g.) was carried out in alcohol (30 c.c.), the temperature being kept below 40° by ice cooling. After standing overnight at 20° the solvent was removed under reduced pressure and then the residue slowly solidified. A saturated solution in ligroin (b. p. 40—60°) deposited prismatic needles of 1-*anilinohex*-1-*en*-3-*one* (8 g.), m. p. 87—88°, after standing for several days at 0° (Found : C, 75·7; H, 7·85. $C_{12}H_{15}ON$ requires C, 76·1; H 8·0%).

1-*Diethylaminohex*-1-*en*-3-*one* (III; R = Pr, R$_1$ = R$_2$ = Et).—A solution of diethylamine (3·7 g.) in ether (10 c.c.) was added to the ketone (5 g.) in ether (20 c.c.) at 0—10°. After this had stood for some hours at 20°, isolation in the usual manner gave the adduct (8 g.), b. p. 105—106·5°/0·4 mm. (Benary, *Ber.*, 1930, **63**, 1573, gives b. p. 137°/15 mm.), $n_{\mathrm{D}}^{20^\circ}$ 1·5237 (Found : C 70·55; H, 11·15. Calc. for $C_{10}H_{19}ON$ : C, 70·9; H, 11·3%).

1-*Piperidinohex*-1-*en*-3-*one* (III; R = Pr, R$_1$R$_2$ = $C_5H_{10}$).—A solution of piperidine (4·5 g.) in alcohol (20 c.c.) was gradually added to the ketone (5 g.) dissolved in alcohol (20 c.c.), the temperature being kept below 20°. Evaporation of the solvent under diminished pressure and distillation of the residue gave 1-*piperidinohex*-1-*en*-3-*one* (6·8 g.) as a pale yellow oil, b. p. 145°/1·5 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·5586 (Found : C, 72·95 ; H, 10·65. $C_{11}H_{19}ON$ requires C, 72·95 ; H, 10·5%). With semicarbazide acetate in aqueous alcoholic solution the *bis-semicarbazone* of *hexane*-1 : 3-*dione* was obtained as crystals, m. p. 203—204°, from methanol (Found : C, 42·35 ; H, 6·95 ; N, 36·7. $C_8H_{16}O_2N_6$ requires C, 42·1 ; H, 7·05 ; N, 36·8%).

1-(o-*Aminoanilino*)-*hex*-1-*en*-3-*one* (VII)—The ketone (0·96 g.) and *o*-phenylenediamine (1·08 g.) were mixed in ether (50 c.c.) at 20° and, after the solvent had evaporated, the solid residue was crystallised from ligroin (b. p. 60—80°) giving 1-(o-*aminoanilino*)-*hex*-1-*en*-3-*one* (1·4 g.) as needles, m. p. 81—82°, which gradually decomposed on keeping (Found : C, 70·4 ; H, 7·85. $C_{12}H_{16}ON_2$ requires C, 70·55 ; H, 7·9%).

### (iv) *Additions to Propenyl Ethynyl Ketone.*

1-*Anilinohexa*-1 : 4-*dien*-3-*one* (IX ; $R_1 = H$, $R_2 = Ph$).—A solution of aniline (5·75 g.) in alcohol (20 c.c.) was added slowly to the ketone (5·75 g.) in alcohol (50 c.c.) the temperature being kept below 40°. After standing at 20° for 3—4 hours, the solution was diluted with water ; resulting oil solidified and on crystallisation from aqueous acetone gave 1-*anilinohexa*-1 : 4-*dien*-3-*one* (8 g.) as small yellow plates, m. p. 117° (Found : C, 77·05 ; H, 7·0 ; N, 7·45. $C_{12}H_{13}ON$ requires C, 77·0 ; H, 7·0 ; N, 7·5%).

1-*Anilinohexan*-3-*one* (X ; $R_1 = H$, $R_2 = Ph$).—1-Anilinohexa-1 : 4-dien-3-one (1 g.) in ethyl acetate (50 c.c.) was shaken in hydrogen at atmospheric pressure and temperature with platinic oxide (100 mg.) until absorption ceased (245 c.c. at 17°/755 mm. Calc. 256 c.c.). The catalyst and solvent were removed and the residue crystallised on keeping at 0° ; on crystallisation from ligroin (b. p. 40—60°) 1-anilinohexan-3-one (0·7 g.) was obtained as needles, m. p. 59·5—60·5°, undepressed on admixture with an authentic specimen prepared by reaction of β-chloroethyl propyl ketone with aniline (Blaise and Maire, *Bull. Soc. chim.*, 1908, **3**, 660, give m. p. 60°).

1-*Piperidinohexa*-1 : 4-*dien*-3-*one* (IX ; $R_1R_2 = C_5H_{10}$).—Piperidine (4·5 g.) and the ketone (5 g.) were mixed in alcohol (60 c.c.) with cooling. Removal of the solvent under reduced pressure and distillation at 75—80° (bath temp.)/$10^{-3}$ mm. gave a pale yellow oil (4 g.) which solidified on keeping at 0°. On crystallisation from ligroin (b. p. 40—60°), 1-*piperidinohexa*-1 : 4-*dien*-3-*one* (2·1 g.) was obtained as lustrous leaflets, m. p. 56—57° (Found : C, 73·65 ; H, 9·4 ; N, 7·55. $C_{11}H_{17}ON$ requires C, 73·7 ; H, 9·55 ; N, 7·8%). The *picrate* formed yellow leaflets, m. p. 143—144°, from methanol (Found : C, 50·0 ; H, 5·0. $C_{17}H_{20}O_8N_4$ requires C, 50·0 ; H, 4·95%).

1-*Piperidinohexan*-3-*one* (X ; $R_1R_2 = C_5H_{10}$).—(a) On gradually adding piperidine (8·5 g.) to β-chloroethyl propyl ketone (6·7 g., for preparation see below) a vigorous reaction tended to occur and was moderated by cooling to 20°. After adding excess of water, the base was isolated by means of ether and on distillation gave 1-*piperidinohexan*-3-*one* (6·8 g.), b. p. 120°/15 mm., $n_{\mathrm{D}}^{14\cdot5^\circ}$ 1·4692 (Found : C, 72·15 ; H, 11·5. $C_{11}H_{21}ON$ requires C, 72·1 ; H, 11·5%). The *picrate* crystallised from alcohol in bright yellow plates, m. p. 94° (Found : C, 49·4 ; H, 5·85. $C_{17}H_{24}O_8N_4$ requires C, 49·5 ; H, 5·85%).

(b) A solution of 1-piperidinohexa-1 : 4-dien-3-one (0·5 g.) in ethyl acetate (50 c.c.) was shaken with platinic oxide (50 mg.) in hydrogen until absorption, which was practically theoretical, was complete. After separation of the catalyst and solvent the residue gave a picrate, m. p. 94°, undepressed on admixture with a specimen prepared by method (a).

1-*Diethylaminohexa*-1 : 4-*dien*-3-*one* (IX ; $R_1 = R_2 = Et$).—The reaction between the ketone (9·4 g.) and diethylamine (7·3 g.) was effected in alcohol (50 c.c.) with ice cooling. After 3 hours at 20°, the alcohol was removed under reduced pressure and distillation of the residual oil gave 1-*diethylaminohexa*-1 : 4-*dien*-3-*one* (10·4 g.) as a pale yellow oil, b. p. 144°/1·5 mm., $n_{\mathrm{D}}^{17^\circ}$ 1·5835 (Found : C, 71·8 ; H, 10·0. $C_{10}H_{17}ON$ requires C, 71·85 ; H, 10·2%). The *picrate* crystallised from methanol in bright yellow plates, m. p. 134° (Found : C, 48·55 ; H, 5·25. $C_{16}H_{20}O_8N_4$ requires C, 48·5 ; H, 5·1%).

1-(p-*Nitroanilino*)-*hexa*-1 : 4-*dien*-3-*one* (IX ; $R_1 = H$, $R_2 = p\text{-}NO_2\cdot C_6H_4$).—A mixture of the ketone (3 g.) and *p*-nitroaniline (4·4 g.) in alcohol (65 c.c.) was kept at room temperature for 6 days and, after precipitation with water and crystallisation from acetone, 1-(p-*nitroanilino*)-*hexa*-1 : 4-*dien*-3-*one* (2 g.) was obtained as bright yellow needles, m. p. 191·5—192·5° (Found : C, 62·2 ; H, 5·55. $C_{12}H_{12}O_3N_2$ requires C, 62·05 ; H, 5·2%).

N:N′-*Bis*-(3-*ketohexa*-1 : 4-*dienyl*)*benzidine*.—When a solution of benzidine (5 g.) in alcohol (40 c.c.) was added to the ketone (5 g.) in alcohol (15 c.c.) the temperature of the mixture rapidly rose to 50° and a yellowish solid separated. The reaction was completed by heating to 80° for 10 minutes and, after cooling, the solid was separated, washed with alcohol and crystallised from acetic acid giving N:N′-*bis*-(3-*ketohexa*-1 : 4-*dienyl*)*benzidine* (5·6 g.) as golden plates, m. p. 247—248° (Found : 77·75 ; H, 6·6. $C_{24}H_{24}O_2N_2$ requires C, 77·45 ; H, 6·5%). With concentrated hydrochloric acid the solid became deep red, the colour reverting to yellow on addition of water.

### *Miscellaneous Addition Reactions.*

1-*Diethylaminohexa*-1 : 3-*dien*-5-*one* (XIII).—Hex-3-en-5-yn-2-one (3 g.) was added to a solution of diethylamine (2·3 g.) in ether (10 c.c.) and, after 24 hours in the dark at room temperature, the ether was removed and the residue distilled to give 1-*diethylaminohexa*-1 : 3-*dien*-5-*one* (2·6 g.) as a yellow viscous oil, b. p. 109°/0·2 mm. (Found : C, 72·0 ; H, 10·2. $C_{10}H_{17}ON$ requires C, 71·8 ; H, 10·25%). The *picrate*, which decomposed in warm solutions, was prepared in cold alcohol and crystallised from cold acetone–ligroin (b. p. 40—60°) in golden plates, m. p. 99—100° (bath preheated to 95°) (Found : C, 48·5 ; H, 5·05. $C_{16}H_{20}O_8N_4$ requires C, 48·5 ; H, 5·1%).

3-*Diethylaminohexa*-1 : 3-*dien*-5-*one* (XIV ; R = H).—Diethylamine (1·95 g.) was added slowly to hex-5-en-3-yn-2-one (2·5 g.) in ether (20 c.c.) with cooling. After 30 minutes at 0° and 2½ hours at 20°, the solvent was removed and the residue distilled in nitrogen giving 3-diethylaminohexa-1 : 3-dien-5-one (1·75 g.) as a pale yellow oil, b. p. 116—118°/0·6 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·5405, which developed a red colour almost immediately after distillation. It decomposed so rapidly (even at 0° in nitrogen and in the presence of hydroquinone) that analysis was not attempted, neither could a solid picrate be obtained. Nevertheless, the light absorption of a freshly distilled sample (see table) provided adequate proof of its structure.

3-*Diethylamino*-2-*methylhexa*-1 : 3-*dien*-5-*one* (XIV ; R = Me).—Diethylamine (2·7 g.) was added very slowly to a cooled solution of 5-methylhex-5-en-3-yn-2-one (4 g.) in ether (25 c.c.). After standing overnight at 20°, evaporation of the ether and distillation of the residue in nitrogen gave 3-*diethylamino*-2-*methylhexa*-1 : 3-*dien*-5-*one* (5 g.) as a pale yellow viscous oil, b. p. 74·5—75°/0·2 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·5363 (Found : C, 72·5 ; H, 10·45. $C_{11}H_{19}ON$ requires C, 72·9 ; H, 10·55%). The *picrate* formed large yellow prisms, m. p. 107·5—109° from methyl alcohol (Found : N, 14·0. $C_{17}H_{22}O_8N_4$ requires N, 13·65%).

3-*Piperidino*-2 : 5-*dipropylfuran* (XVI).—The keto-alcohol (2·8 g.) and piperidine (1·4 g.) were mixed in ether (20 c.c.) with cooling (ice) and the mixture was set aside at 20° for 2 days. The product was taken up in ether ; the basic material was extracted with N-hydrochloric acid and, after further extraction of the aqueous solution, it was liberated with 2N-sodium hydroxide. This procedure gave 3-*piperidino*-2 : 5-*dipropylfuran* (1·8 g.), b. p. 110°/1 mm., 83°/0·15 mm., $n_{\mathrm{D}}^{17^\circ}$ 1·4909 (Found : C, 76·45 ; H, 10·45. $C_{15}H_{25}ON$ requires C, 76·5 ; H, 10·7%). The *hydrochloride*, prepared with dry hydrogen chloride in ethereal solution, sublimed at 70° (bath temp.)/$10^{-4}$ mm. and had m. p. 145·5—146° (decomp.) (Found : N, 5·45. $C_{15}H_{26}ONCl$ requires N, 5·15%).

### *Intermediates and Spectrographic Reference Compounds.*

*β-Chloroethyl Propyl Ketone* (cf., Kenner and Statham, *Ber.*, 1936, **69**, 16).—*n*-Butyryl chloride (126 g.) was stirred and cooled (ice–salt) and freshly powdered aluminium chloride (158 g.) was added during 30 minutes and stirring and cooling were continued for a further 50 minutes. Dry ethylene was then passed in, the temperature being kept at 20°, until 33 g. had been absorbed after which the mixture was stirred for 30 minutes at 20°. The product was isolated by treatment with ice and extraction with chloroform, and β-chloroethyl propyl ketone (127 g., 80%) was obtained having b. p. 67—68°/11 mm. (Blaise and Maire, *Bull. Soc. chim.*, 1906, **3**, 270, give b. p. 73°/10 mm., 68°/9 mm.).

1-*Piperidino*-1-*butene* (1).—This was prepared according to Mannich and Davidsen (*Ber.*, 1936, **69**, 2106) and had b. p. 84—85°/21 mm., $n_{\mathrm{D}}^{19\cdot5°}$ 1·4860. On dissolution of 1 g. in M-HCl (100 c.c.) the solution showed no absorption with $E^{1\%}_{1\,\mathrm{cm.}} > 20$ at 2280 A. After adding a slight excess of M-KOH the original compound (0·6 g.) having b. p. 76—79°/18 mm., $n_{\mathrm{D}}^{22°}$ 1·4845 was recovered.

1-*Diethylaminobutadiene* (2).—The general description of this compound and of its preparation given in the literature (Langebeck *et al.*, *Ber.*, 1942, **75**, 235; cf., Mannich, Handke, and Röth, *Ber.*, 1936, **69**, 2112) does not appear to be satisfactory. It has been found that by treating anhydrous diethylamine with crotonaldehyde at −10° in the presence of anhydrous potassium carbonate the above amine is produced directly in 50% yield, but it polymerises extensively on distillation or on standing at 20°. It has b. p. 74°/20 mm., $n_{\mathrm{D}}^{19°}$ 1·5232. Its structure was confirmed by hydrogenation in *cyclo*hexane with platinic oxide to *N*-diethylbutylamine (b. p. 136—137°), and by the formation of anthraquinone by condensation with α-naphthaquinone, in rather higher yield than that claimed by Langebeck *et al.* (*loc. cit.*).

N-*Diethylcrotonamide* (10).—Prepared from crotonyl chloride (7 g.) and excess diethylamine in dry ether, the *amide* (8·5 g.) had b. p. 52—55°/0·6 mm., $n_{\mathrm{D}}^{23°}$ 1·4735 (Found : N, 10·3. $C_8H_{15}ON$ requires N, 9·95%).

*Ethyl β-Diethylaminocrotonate* (3) (cf. Kuckert, *Ber.*, 1885, **18**, 618).—A mixture of ethyl acetoacetate (21 g.) and diethylamine (9 g.) was allowed to stand with anhydrous sodium sulphate during 20 days at 20°. The amino-ester (16 g.) having b. p. 93—95°/0·6 mm., $n_{\mathrm{D}}^{23°}$ 1·5115, was obtained.

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IMPERIAL COLLEGE OF SCIENCE AND TECHONOLOGY, LONDON, S.W. 7.

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