Synthesis and Thermal Reaction of Pyridinium 3,3-Diacyl-1-benzoylallylides [3,3-Diacyl-1-benzoyl-1-(1-pyridinio)prop-2-enides]: Formation of Indolizine Derivatives

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Pyridinium 3,3-diacyl-1-benzoylallylides [(IIIa—e), (IV), and (V)] are prepared by the reaction of pyridinium phenacylides with 2,2-diacyl-1-ethoxyethylenes. Refluxing compounds (IIIa), (IIIb), and (IV) in xylene provides 1-acyl-3-benzoylindolizines [(VI), (VII), and (IX)] in poor yields; similar treatment of the 2-methylpyridinium congeners (IIIc—e) affords 1,3-diacetyl-2-phenylindolizines [(X)—(XII)], accompanied by small amounts of 1-acetyl-3-benzoylindolizines [(VI)—(VIII)].

PYRIDINIUM ALLYLIDES [1-(1-pyridinio)prop-2-enides] have been shown to undergo a number of cyclisation reactions giving various indolizines.[1-6] In this paper the synthesis and thermochemical behaviour of a new type of stabilised pyridinium ylide, the pyridinium 3,3-diacyl-1-benzoylallylides [(III)—(V)], are described.

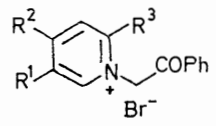
Compounds (IIIa—e) were synthesised by the reaction of the pyridinium phenacylides (IIa—e), generated *in situ*, with 2,2-diacyl-1-ethoxyethylenes.† For example, pyridinium phenacylide (IIa) [prepared by passing an ethanolic solution of 1-phenacylpyridinium bromide (Ia) through an ion-exchange resin] reacted in ethanolic solution with 3-ethoxymethylenepentane-2,4-dione [7] at room temperature to give pyridinium 3,3-diacetyl-1-benzoylallylide (IIIa) in high yield. Compounds (IV) and (V) had been synthesised in much the same manner by reaction of the ylides (II) with diethyl ethoxymethylenemalonate [8] or ethyl 2-cyano-3-ethoxyacrylate.[9] This reaction may be interpreted in terms of an addition–elimination mechanism, involving nucleophilic attack of a pyridinium ylide on an unsaturated carbon atom followed by elimination of ethanol.[10]

These compounds were characterised by analytical and spectroscopic data (see Experimental section). Specifically, the i.r. spectra of compounds (IIIa—e) showed no strong absorption above 1630 cm^{-1}, suggesting that the negative charge is delocalised over all the carbonyl groups. This was further supported by the n.m.r. spectra, in each of which a signal due to two acetyl groups appeared as a sharp singlet at τ *ca.* 7·8 (6H); presumably rapid rotation around the delocalised carbon–carbon double bond is possible.[11] Similar behaviour was exhibited by compound (IV), which showed an i.r. carbonyl band at 1660 cm^{-1} and a diffuse, broad n.m.r. signal due to the O·CH_2·CH_3 system. A diagnostically important feature in the n.m.r. spectra of these compounds was the pronounced deshielding of the olefinic

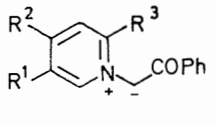
† Recently similar reactions of dimethylsulphoxonium methylide and dimethylsulphoximide with 2,2-diacyl-1-ethoxyethylenes have been reported (Y. Tamura, T. Miyamoto, H. Taniguchi, K. Sumoto, and M. Ikeda, *Tetrahedron Letters*, 1973, 1729).

[1] Y. Tamura, N. Tsujimoto, Y. Sumida, and M. Ikeda, *Tetrahedron*, 1972, **28**, 21.
[2] Y. Tamura, Y. Sumida, and M. Ikeda, *Chem. and Pharm. Bull.* (*Japan*), 1973, **21**, 1139.
[3] Y. Tamura, Y. Sumida, and M. Ikeda, *Chem. and Pharm. Bull* (*Japan*), 1972, **20**, 1058.
[4] E. Pohjala, *Tetrahedron Letters*, 1972, 2585.
[5] T. Sasaki, K. Kanematsu, A. Kakehi, and G. Ito, *Tetrahedron*, 1972, **28**, 4947.
[6] D. I. Schütze and F. Kröhnke, *Annalen.*, 1972, **765**, 20.
[7] L. Claisen, *Annalen*, 1897, **297**, 1.
[8] L. Claisen, *Ber.*, 1893, **26**, 2729.
[9] de Bollemont, *Compt. rend.*, 1899, **128**, 1340.
[10] S. Patai and Z. Rappoport, ' The Chemistry of Alkenes,' ed. S. Patai, Interscience, London, 1964, p. 525.
[11] Y. Shvo and H. Shaman-Atidi, *J. Amer. Chem. Soc.*, 1969, **91**, 6683, 6689.

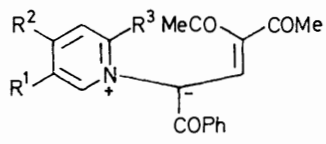
proton (τ *ca.* 1·80—2·25), attributed to the combined anisotropic, mesomeric, and inductive effects of the 3-acyl groups.



(Ia-e)

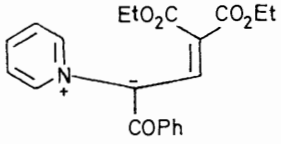


(IIa-e)

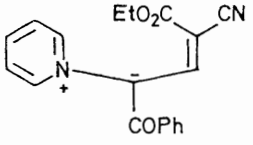


(IIIa-e)

	R^1	R^2	R^3
a;	H	H	H
b;	H	Me	H
c;	H	H	Me
d;	H	Me	Me
e;	Me	H	Me

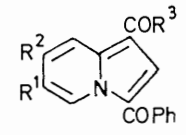


(IV)

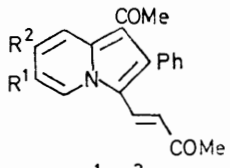


(V)

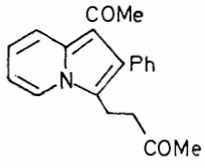
Refluxing the ylide (IIIa) in xylene for 10 h gave large quantities of intractable material, from which 1-acetyl-3-benzoylindolizine (VI) was isolated in low yield (6%). Similarly, the 4-methylpyridinium allylide (IIIb) gave the indolizine (VII) in only 0·5% yield. The structures of these indolizines were established by direct comparison with authentic samples, prepared by 1,3-dipolar cycloadditions [12] of the corresponding pyridinium phenacylides to acetylacetylene. The bisethoxycarbonyl derivative (IV) behaved analogously under the same conditions, affording ethyl 3-benzoylindolizine-1-carboxylate (IX) [12] in 20% yield. These results parallel those obtained for the thermal reactions of pyridinium 3-benzoyl-2-phenylallylide [1] and pyridinium 3-ethoxycarbonyl-2-phenylallylide.[2]



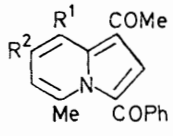
(VI) $R^1 = R^2 = H, R^3 = Me$
(VII) $R^1 = H, R^2 = R^3 = Me$
(VIII) $R^2 = H, R^1 = R^3 = Me$
(IX) $R^1 = R^2 = H, R^3 = OEt$



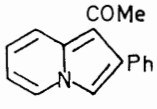
(X) $R^1 = R^2 = H$
(XI) $R^1 = H, R^2 = Me$
(XII) $R^2 = H, R^1 = Me$



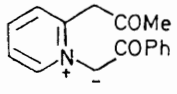
(XIII)



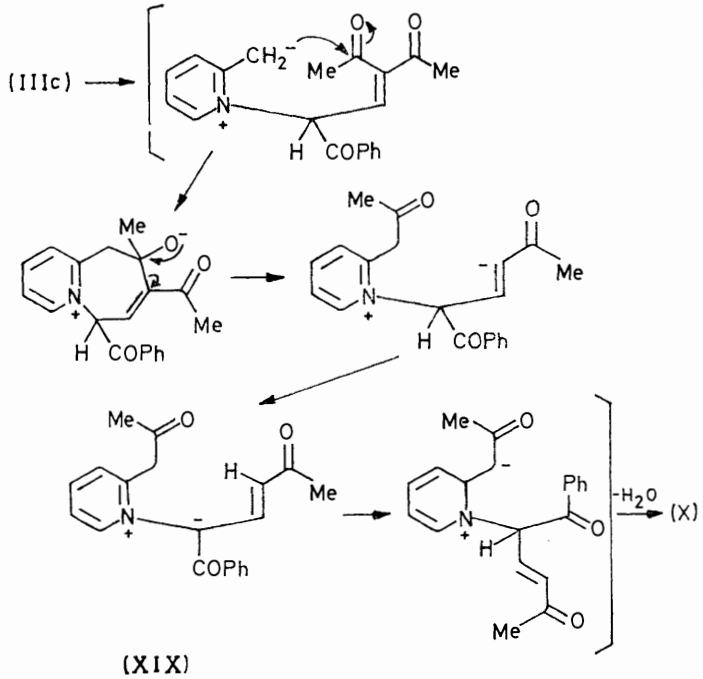
(XIV) $R^1 = R^2 = H$
(XV) $R^1 = H, R^2 = Me$
(XVI) $R^2 = H, R^1 = Me$



(XVII)



(XVIII)



(XIX)

[1] T. Sasaki, K. Kanematsu, Y. Yukimoto, and S. Ochiai, *J. Org. Chem.*, 1971, **36**, 813.

In contrast, similar treatment of the 2-methylpyridinium ylide (IIIc) afforded two indolizines, (X) and (VI), in 30 and 2% yield, respectively. The structure of the major product (X) was assigned on the basis of analysis, spectral data, and the product of catalytic hydrogenation. The n.m.r. spectrum showed two methyl singlets (τ 7·95 and 8·12), a doublet (1H) at τ 3·94 with a large coupling constant (16·5 Hz), an aromatic proton multiplet at τ 2·2—3·1, and two doublets at τ 1·54 (*J* 6·5 Hz, 5-H) and 1·33 (*J* 9 Hz, 8-H). Catalytic hydrogenation over 5% Pd–C gave the dihydro-derivative (XIII), in the n.m.r. spectrum of which the vinylic proton signal had disappeared and a four-proton signal was present at τ 6·8—7·7 as an A_2B_2-type multiplet. The u.v. spectrum of (XIII) closely resembles that of 1-acetyl-2-phenylindolizine (XVII), synthesised by Chichibabin cyclisation of the ylide (XVIII).[13] Assignment of the *trans*-stereochemistry in (X) was made on the basis of the large olefinic proton coupling constant. The formation of (X) may be rationalised as proceeding by migration of the acetyl group to give the intermediate (XIX), followed by Chichibabin cyclisation.

Similarly, the 2,4-dimethylpyridinium derivative (IIId) was transformed into the indolizines (XI) and (VII) in 32 and 10% yield, and the 2,5-dimethyl derivative (IIIe) into (XII) and (VIII) in 33 and 3%, yield. The other possible indolizine isomers (XIV)—(XVI) were not detected in all three cases. The specific formation of the indolizines (VI)—(VIII) is unexpected and we can at present offer no explanation.

The 3-cyano-3-ethoxycarbonyl-derivative (V) was remarkably stable; it was unchanged after refluxing for 20 h in xylene. Some decomposition of (V) occurred in refluxing tetralin but no indolizine derivative was detected.

EXPERIMENTAL

N.m.r. spectra were determined with a Hitachi R-20A spectrometer (tetramethylsilane as internal standard). I.r. spectra were recorded with a Hitachi EPI-G2 spectrophotometer, and u.v. spectra with a Hitachi 124 spectrophotometer. Mass spectra were obtained with a Hitachi RMU-6D instrument with a direct inlet system operating at 70 eV. Preparative layer chromatography (p.l.c.) was carried out on Merck alumina PF_{254}.

Pyridinium 3,3-*Diacetyl*-1-*benzoylallylides*.—An ethanolic solution of a pyridinium phenacylide [prepared by passing an ethanolic solution of a 1-phenacylpyridinium bromide (5 mmol) through Amberlite IRA-410 ion-exchange resin] was added to a vigorously stirred solution of 3-ethoxymethylenepentane-2,4-dione [7] (5 mmol) in ethanol. The mixture was stirred at room temperature for 3 h. The solvent was distilled off to leave yellow or orange crystals, which were recrystallised from ethanol–light petroleum (b.p. 30—60°). *Pyridinium* 3,3-*diacetyl*-1-*benzoylallylide* (IIIa) (75%) formed orange needles, m.p. 187—189° (decomp.) (Found: C, 74·2; H, 5·6; N, 4·7%; M^+, 307. $C_{19}H_{17}NO_3$ requires C, 74·25; H, 5·6; N, 4·7%; *M*, 307); $\nu_{max.}$ (KCl) 1625w, 1580m, 1495s, and 1245s cm^{-1}; $\lambda_{max.}$ (EtOH) 249·5, 282sh, and 374·5 nm (log ε 3·99, 3·87, and 4·35); τ ($CDCl_3$) 1·60 (2H, dd, *J* 1·5 and 6·5 Hz, α-protons of pyridine), 1·82 (1H, dd, *J* 1·5 and 7 Hz, γ-proton of pyridine), 2·0—2·7 (7H, m, other aromatic protons), 2·18 (1H, s, olefinic proton), and 7·89 (6H, s, 2 × Ac). 4-*Methylpyridinium* 3,3-*diacetyl*-1-*benzoylallylide* (IIIb) (54%) formed yellow needles, m.p. 212—214° (decomp.) (Found: C, 74·6; H, 5·9; N, 4·25%; M^+, 321. $C_{20}H_{19}NO_3$ requires C, 74·7; H, 6·0; N, 4·4%; *M*, 321); $\nu_{max.}$ (KCl) 1610s, 1590s, 1505s, and 1255s cm^{-1}; $\lambda_{max.}$ (EtOH) 245·5, 281·5, and 376 nm (log ε 4·23, 4·09, and 4·56); τ ($CDCl_3$) 1·80 (2H, d, *J* 7 Hz, α-protons of pyridine), 2·21 (1H, s, olefinic proton), 2·25—2·75 (7H, m, other aromatic protons), 7·39 (3H, s, CH_3), and 7·91 (6H, s, 2 × Ac). 2-*Methylpyridinium* 3,3-*diacetyl*-1-*benzoylallylide* (IIIc) (65%) formed orange needles, m.p. 148—150° (decomp.) (Found: C, 75·0; H, 6·2; N, 4·45%; M^+, 321. $C_{20}H_{19}NO_3$ requires C, 74·7; H, 6·0; N, 4·4%; *M*, 321); $\nu_{max.}$ (KCl) 1640w, 1615m, 1590s, and 1245s cm^{-1}; $\lambda_{max.}$ (EtOH) 260 and 374·5 nm (log ε 4·25 and 4·48); τ ($CDCl_3$) 1·7—2·05 (2H, m, α- and γ-protons of pyridine), 2·20 (1H, s, olefinic proton), 2·25—2·65 (7H, m, other aromatic protons), 7·29 (3H, s, CH_3), and 7·98 (6H, s, 2 × Ac). 2,4-*Dimethylpyridinium* 3,3-*diacetyl*-1-*benzoylallylide* (IIId) (27%) formed orange needles, m.p. 156—158° (decomp.) (Found: C, 75·1; H, 6·4; N, 4·1%; M^+, 335. $C_{21}H_{21}NO_3$ requires C, 75·2; H, 6·3; N, 4·2%; *M*, 335); $\nu_{max.}$ (KCl) 1630w, 1590s, 1500s, and 1245s cm^{-1}; $\lambda_{max.}$ (EtOH) 225sh, 261, and 376 nm (log ε 3·98, 3·81, and 4·15); τ ($CDCl_3$) 2·07 (1H, d, *J* 6·5 Hz, α-proton of pyridine), 2·22 (1H, s, olefinic proton), 2·25—2·80 (7H, m, other aromatic protons), 7·37 (3H, s, CH_3), 7·52 (3H, s, CH_3), and 7·96 (6H, s, 2 × Ac). 2,5-*Dimethylpyridinium* 3,3-*diacetyl*-1-*benzoylallylide* (IIIe) (82%) formed yellow pillars, m.p. 154—156° (decomp.) (Found: C, 74·2; H, 6·4; N, 4·1%; M^+, 335. $C_{21}H_{21}NO_3$,0·2H_2O requires C, 74·4; H, 6·4; N, 4·1%; *M*, 335); $\nu_{max.}$ (KCl) 1610m, 1585m, 1500s, and 1250s cm^{-1}; $\lambda_{max.}$ (EtOH) 221sh, 248sh, 276, and 375 nm (log ε 4·14, 4·05, 4·16, and 4·58); τ ($CDCl_3$) 1·9—2·15 (2H, m, α- and γ-protons of pyridine), 2·20 (1H, s, olefinic proton), 2·25—2·65 (6H, m, other aromatic protons), 7·33 (3H, s, CH_3), 7·60 (3H, s, CH_3), and 7·98 (6H, s, 2 × Ac).

Pyridinium 1-*Benzoyl*-3,3-*bisethoxycarbonylallylide* (IV).—By use of a similar procedure this compound was obtained from pyridinium phenacylide and diethyl ethoxymethylenemalonate [8] in 16% yield as a red viscous oil. This oil was used for further reaction after washing with light petroleum (b.p. 30—60°); $\nu_{max.}$ ($CHCl_3$) 1660s cm^{-1}; $\lambda_{max.}$ (EtOH) 244·5, 387·5, and 448 nm (log ε 4·05, 4·35, and 4·35); τ ($CDCl_3$) 1·55 (2H, d, *J* 6 Hz, α-protons of pyridine), 1·90 (1H, s, olefinic proton), 2·1—2·65 (8H, m, other aromatic protons), 5·7—6·5br (4H, 2 × O·CH_2·CH_3), and 8·90 (6H, t, *J* 7 Hz, 2 × O·CH_2·CH_3).

Pyridinium 1-*Benzoyl*-3-*cyano*-3-*ethoxycarbonylallylide* (V).—By a similar procedure this compound was obtained from pyridinium phenacylide and ethyl 2-cyano-3-ethoxyacrylate [9] in 50% yield as yellow needles, m.p. 230—232° (decomp.) [from ethanol–light petroleum (b.p. 30—60°)] (Found: C, 71·0; H, 5·0; N, 8·8%; M^+, 320. $C_{19}H_{16}N_2O_3$ requires C, 71·2; H, 5·0; N, 8·75%; *M*, 320); $\nu_{max.}$ (KCl) 2170s, 1680m, 1515s, and 1230s cm^{-1}; $\lambda_{max.}$ (EtOH) 223sh, 247, and 360·5 nm (log ε 4·34, 4·23, and 4·77); τ ($CDCl_3$) 1·49 (2H, dd, *J* 1 and 6·5 Hz, α-protons of pyridine), 1·60—1·90 (1H, m, γ-proton of pyridine), 1·81 (1H, s, olefinic proton), 1·98br (2H, d, *J* 6·5 Hz, β-protons of pyridine), 2·2—2·7 (5H, m, Ph), 5·84 (2H, q, *J* 7 Hz, O·CH_2·CH_3), and 8·76 (3H, t, *J* 7 Hz, O·CH_2·CH_3).

[13] I. Dainis, *Austral. J. Chem.*, 1972, **25**, 1003.

Thermal Reactions.—(a) *Pyridinium* 3,3-*diacetyl*-1-*benzoylallylide* (IIIa). A suspension of (IIIa) (100 mg) in xylene (15 ml) was heated under reflux for 10 h until a clear solution was obtained. The solvent was evaporated off under reduced pressure. The residue was purified by p.l.c. with benzene to give pale yellow needles (5 mg, 6%) of 1-*acetyl*-3-*benzoylindolizine* (VI), m.p. 145—147° (from ethanol–water) (Found: C, 77·3; H, 4·9; N, 5·3%; M^+, 263. $C_{17}H_{18}NO_2$ requires C, 77·55; H, 5·0; N, 5·3%; *M*, 263); $\nu_{max.}$ (KCl) 1650s, 1610s, and 1500s cm^{-1}; $\lambda_{max.}$ (EtOH) 229, 236sh, 254, 284sh, 292, 336sh, 352·5, and 365sh nm (log ε 4·12, 4·11, 4·14, 3·96, 4·00, 4·14, 4·16, and 4·12); τ ($CDCl_3$) 0·00 (1H, d, *J* 7 Hz, 5-H), 1·33 (1H, d, *J* 8·5 Hz, 8-H), 2·0—2·55 (6H, m, 2-H and Ph), 2·6—3·0 (2H, m, 6- and 7-H), and 7·51 (3H, s, Ac).

(b) 4-*Methylpyridinium* 3,3-*diacetyl*-1-*benzoylallylide* (IIIb). Compound (IIIb) (480 mg) was treated as in (a) to give 1-*acetyl*-3-*benzoyl*-7-*methylindolizine* (VII) (2·2 mg) as yellow needles, m.p. 175—176° (from ethanol–water) (Found: C, 78·3; H, 5·6; N, 4·9%; M^+, 277. $C_{18}H_{15}NO_2$ requires C, 78·0; H, 5·45; N, 5·05%; *M*, 277); $\nu_{max.}$ (KCl) 1645m, 1610s, and 1505s cm^{-1}; $\lambda_{max.}$ (EtOH) 232sh, 237·5, 250·5sh, 286sh, 296, 337sh, and 359 nm (log ε 4·20, 4·22, 4·21, 3·93, 4·01, 4·21, and 4·26); τ ($CDCl_3$) 0·12 (1H, d, *J* 7 Hz, 5-H), 1·55br (1H, s, 8-H), 2·1—2·6 (6H, m, 2-H and Ph), 3·01 (1H, dd, *J* 2 and 7 Hz, 6-H), 7·52 (3H, s, Ac), and 7·57 (3H, s, CH_3).

(c) 2-*Methylpyridinium* 3,3-*diacetyl*-1-*benzoylallylide* (IIIc). A suspension of (IIIc) (160 mg) in xylene (20 ml) was heated under reflux for 3 h. The solvent was evaporated off under reduced pressure. T.l.c. [alumina GF_{254}; chloroform–methanol (10 : 1)] showed that two products were present. These were separated by p.l.c. The major product crystallised from ethanol–water to give yellow needles (45 mg, 30%) of 2-(1-*acetyl*-2-*phenylindolizin*-3-*yl*)-*vinyl methyl ketone* (X), m.p. 142—143° (Found: C, 79·4; H, 5·7; N, 4·7%; M^+, 303. $C_{20}H_{17}NO_2$ requires C, 79·2; H, 5·65; N, 4·6%; *M*, 303); $\nu_{max.}$ (KCl) 1640m and 1605s cm^{-1}; $\lambda_{max.}$ (EtOH) 234, 272, 315, 370·5, and 413sh nm (log ε 4·32, 3·98, 3·98, 4·06, and 3·93); τ ($CDCl_3$) 1·33 (1H, d, *J* 9 Hz, 8-H), 1·54 (1H, d, *J* 6·5 Hz, 5-H), 2·2—3·1 (8H, m, 6-H, 7-H, Ph, and olefinic proton), 3·94 (1H, d, *J* 16·5 Hz, olefinic proton), and 7·95 and 8·12 (each 3H, s, Ac).

The minor product (2·4 mg) was 1-acetyl-3-benzoylindolizine (VI).

(d) 2,4-*Dimethylpyridinium* 3,3-*diacetyl*-1-*benzoylallylide* (IIId). By treatment as described for the thermal reaction of (IIIc), the ylide (IIId) (160 mg) gave two products. The major product crystallised from ethanol–water to give yellow needles (60 mg, 32%) of 2-(1-*acetyl*-7-*methyl*-2-*phenylindolizin*-3-*yl*)*vinyl methyl ketone* (XI), m.p. 125—126° (Found: C, 79·1; H, 6·1; N, 4·3%; M^+, 317. $C_{21}H_{19}NO_2$ requires C, 79·5; H, 6·0; N, 4·4%; *M*, 317); $\nu_{max.}$ (KCl) 1640m, 1600m, and 1570s cm^{-1}; $\lambda_{max.}$ (EtOH) 226·5, 271·5, 319, 369, and 408·5 nm (log ε 4·42, 4·16, 4·13, 4·24, and 4·18); τ ($CDCl_3$) 1·4—1·7 (2H, m, 5- and 8-H), 2·25—2·8 (6H, m, Ph, and olefinic proton), 3·10 (1H, dd, *J* 7 Hz, 6-H), 3·93 (1H, d, *J* 16·5 Hz, olefinic proton), 7·67 (3H, s, CH_3), and 7·93 and 8·12 (each 3H, s, Ac).

The minor product (16 mg) was 1-acetyl-3-benzoyl-7-methylindolizine (VII).

(e) 2,5-*Dimethylpyridinium* 3,3-*diacetyl*-1-*benzoylallylide* (IIIe). In a similar way the ylide (IIIe) (160 mg) gave two products. The major product crystallised from ethanol–water to give yellow needles (62 mg, 33%) of 2-(1-*acetyl*-6-*methyl*-2-*phenylindolizin*-3-*yl*)*vinyl methyl ketone* (XII), m.p. 161—163° (Found: C, 79·1; H, 6·1; N, 4·4%; M^+, 317. $C_{21}H_{19}NO_2$ requires C, 79·4; H, 6·0; N, 4·4%; *M*, 317); $\nu_{max.}$ (KCl) 1640m, 1605m, and 1575s cm^{-1}; $\lambda_{max.}$ (EtOH) 230·5, 272·5, 318·5, 370, and 422sh nm (log ε 4·33, 4·01, 4·08, 4·18, and 3·95); τ ($CDCl_3$) 1·43 (1H, d, *J* 9 Hz, 8-H), 1·74br (1H, s, 5-H), 2·25—2·95 (7H, m, 7-H, Ph, and olefinic proton), 3·99 (1H, d, *J* 16 Hz, olefinic proton), 7·62 (3H, s, CH_3), and 7·96 and 8·13 (each 3H, s, Ac).

The minor product (5 mg) was 1-*acetyl*-3-*benzoyl*-6-*methylindolizine* (VIII), pale yellow needles, m.p. 132—133° (from ethanol–water) (Found: C, 77·9; H, 5·4; N, 4·9%; M^+, 277. $C_{18}H_{15}NO_2$ requires C, 78·0; H, 5·45; N, 5·05%; *M*, 277); $\nu_{max.}$ (KCl) 1645m, 1615s, and 1510s cm^{-1}; $\lambda_{max.}$ (EtOH) 232, 253, 261sh, 285sh, 293·5, 347, and 367sh nm (log ε 4·18, 4·22, 4·20, 4·07, 4·12, 4·21, and 4·19); τ ($CDCl_3$) 0·17br (1H, s, 5-H), 1·44 (1H, d, *J* 9 Hz, 8-H), 2·05—2·75 (7H, m, 2-H, 7-H, and Ph), 7·51 (3H, s, Ac), and 7·55 (3H, s, CH_3).

(f) *Pyridinium* 1-*benzoyl*-3,3-*bisethoxycarbonylallylide* (IV). A suspension of the oily compound (IV) (95 mg) in xylene (15 ml) was heated under reflux for 15 h until a clear solution was obtained. Work-up as described for (Xa) gave yellow needles (19 mg) of ethyl 3-benzoylindolizine-1-carboxylate (IX), m.p. 77—78° (from n-hexane) (lit.,[5] 81—82°).

Catalytic Hydrogenation of 2-(1-*Acetyl*-2-*phenylindolizin*-3-*yl*)*vinyl Methyl Ketone* (X).—Compound (X) (70 mg) was hydrogenated in ethanol (10 ml) over 5% Pd–C (50 mg) at atmospheric pressure and room temperature. The mixture was filtered and concentrated. The oily residue was purified by p.l.c. with benzene–chloroform (10 : 1) to give pale yellow needles (30 mg, 43%) of 2-(1-*acetyl*-2-*phenylindolizin*-3-*yl*)*ethyl methyl ketone* (XIII), m.p. 109—110° (from ethanol–water) (Found: C, 78·6; H, 6·4; N, 4·4%; M^+ 305. $C_{20}H_{19}NO_2$ requires C, 78·7; H, 6·3; N, 4·6%; *M* 305); $\nu_{max.}$ (KCl) 1710s and 1615s cm^{-1}; $\lambda_{max.}$ (EtOH) 235·5, 327sh, 361, and 380·5sh nm (log ε 4·39, 3·80, 4·07, and 3·97); τ ($CDCl_3$) 1·44 (1H, d, *J* 9 Hz, 8-H), 2·05 (1H, d, *J* 7 Hz, 5-H), 2·5—3·2 (7H, m, 6-H, 7-H, and Ph), 6·8—7·7 (4H, m, $[CH_2]_2$), and 7·99 and 8·12 (each 3H, s, Ac).

1-*Acetyl*-2-*phenylindolizine* (XVII).—Bragg's [14] procedure was used. A solution of 2-acetonylpyridine (1·35 g) and phenacyl bromide (1 g) in acetone (5 ml) was heated under reflux for 15 h. The solvent was evaporated off and 2N-hydrochloric acid (5 ml) was added. The solution was extracted with ether and the dried extract was concentrated to give an oily residue, which was purified by p.l.c. with benzene. Recrystallisation from light petroleum (b.p. 30—60°) gave pale yellow *crystals*, m.p. 53—55° (Found: C, 81·55; H, 5·7; N, 5·9. $C_{16}H_{13}NO$ requires C, 81·7; H, 5·6; N, 5·95%); $\nu_{max.}$ (KCl) 1630m and 1610s cm^{-1}; $\lambda_{max.}$ (EtOH) 236, 321sh, 353·5, and 370sh nm (log ε 4·56, 3·99, 4·28, and 4·17); τ ($CDCl_3$) 1·54 (1H, d, *J* 9 Hz, 8-H), 2·03 (1H, dd, *J* 1 and 6·5 Hz, 5-H), 2·6 (5H, s, Ph), 2·65—3·05 (1H, m, 7-H), 2·84 (1H, s, 3-H), 3·24 (1H, td, *J* 1·5 and 6·5 Hz, 6-H) and 7·94 (3H, s, Ac).

1-*Acetyl*-3-*benzoylindolizine* (VI).—Potassium carbonate (345 mg) was added to a solution of 1-phenacylpyridinium bromide (Ia) (556 mg) in dimethylformamide (10 ml). After 5 min, acetylacetylene (272 mg) was added and the mixture was stirred for 3 h at room temperature. The solvent was evaporated off under reduced pressure and the residue was dissolved in chloroform; the solution was filtered to remove inorganic material. The filtrate was

[14] D. R. Bragg and D. G. Wibberley, *J. Chem. Soc.*, 1963, 3277.

concentrated and the residue chromatographed on alumina. Elution with benzene–chloroform (5 : 1) gave pale yellow needles of (VI) (152 mg, 29%), m.p. 145—146°.

1-*Acetyl*-3-*benzoyl*-7-*methylindolizine* (VII).—In a similar manner, compound (VII) (140 mg, 25%) was obtained from 1-phenacyl-4-methylpyridinium bromide (Ib) (584 mg) and acetylacetylene (272 mg) as yellow needles, m.p. 173—174° (from ethanol–water).

1-*Acetyl*-3-*benzoyl*-6-*methylindolizine* (VIII) *and* 1-*Acetyl*-3-*benzoyl*-8-*methylindolizine*.—Under similar conditions, the reaction of 1-phenacyl-3-methylpyridinium bromide (584 mg) with acetylacetylene (272 mg) gave two products, which were separated by p.l.c. using benzene–chloroform (10 : 1). One was 1-acetyl-3-benzoyl-6-methylindolizine (VII) (26 mg, 5%); the other was 1-*acetyl*-3-*benzoyl*-8-*methylindolizine* (44 mg, 8%), m.p. 77—78·5° (from ethanol–water) (Found: C, 77·7; H, 5·4; N, 5·2. $C_{18}H_{15}NO_2$ requires C, 78·0; H, 5·45; N, 5·05%); $\nu_{max.}$ (KCl) 1670m, 1620s, and 1505s cm^{-1}; $\lambda_{max.}$ (EtOH) 236, 264, 292, 337, and 370 nm (log ε 4·16, 4·15, 3·89, 4·06, and 4·11); τ ($CDCl_3$) 0·06 (1H, d, J 6 Hz, 5-H), 2·0—2·6 (6H, m, 2-H and Ph), 2·65—2·9 (1H, m, 7-H), 3·04 (1H, d, J 7 Hz, 6-H), 7·28 (3H, s, CH_3), and 7·48 (3H, s, Ac).

[3/852 *Received*, 25*th April*, 1972]