Base-catalysed Rearrangements involving Ylide Intermediates. Part 8.[†] The Preparation and Some Reactions of Stable Ammonium Ylides[‡]

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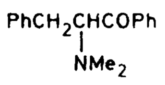
The carbonyl-stabilised ammonium ylides (3), (12a—n), and (14a—c) were obtained from the reaction of the corresponding ammonium halides (1), (13a—n), and (15a—c) with sodium hydroxide in water or aqueous methanol. The ylides, which were characterised by their molecular formulae and spectroscopic properties, regenerated quaternary ammonium bromides on treatment with hydrobromic acid. In general the reactions of the ammonium ylides resemble those of the corresponding sulphonium ylides. Thus ylides having a suitable migrating group ($ArCH_2$) undergo a Stevens [1,2] rearrangement on heating, and other ylides fragment to give a tertiary amine and products containing the PhCOCH grouping. A number of ylides reacted with dimethyl acetylenedicarboxylate to give the furans (32). The ylides (14b and c) with phenyl isocyanate gave the phenylcarbamoyl-substituted ylides (35).

THE Stevens [1,2] anionic rearrangement was discovered in 1928 when T. S. Stevens and his co-workers reported[1] that treatment of benzyldimethyl(phenacyl)ammonium bromide (1) with warm, aqueous sodium hydroxide gave the amino-ketone (2). Stevens subsequently proposed[2] that the ylide (3) was an intermediate in the reaction (1)→(2), but ammonium ylides closely analogous to (3) which are able to undergo a [1,2] rearrangement had not been isolated before the work described in this paper[3] was initiated, although stable phosphonium[4] and sulphonium[5] ylides were well known. Furthermore, the acidity constants for the sulphonium salt (4a) (pK_a 6.66) and the phosphonium salt (4b) (pK_a 7.75) are significantly lower[6] than that of the analogous ammonium salt (4c) (pK_a 9.8) suggesting that the stabilities of the corresponding ylides (5) would decrease in the order (5a) > (5b) ≫ (5c).

$PhCH_2\overset{+}{N}Me_2CH_2COPh\ \ \overset{-}{Br}$

(1)

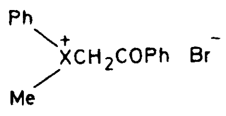


$PhCH_2\underset{NMe_2}{CH}COPh$

(2)

$PhCH_2\overset{+}{N}Me_2\overset{-}{C}HCOPh$

(3)



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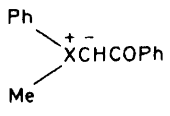
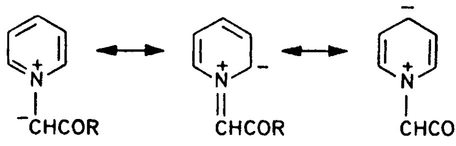


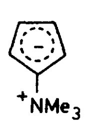
(5)

a ; X = S
b ; X = PMe
c ; X = NMe

It had been shown[4,5] that $\overset{+}{P}-\overset{-}{C}$ and $\overset{+}{S}-\overset{-}{C}$ bond lengths were significantly shorter in these ylides than the normal P–C and S–C single bond lengths, in accord with the view that d_π–p_π bonding might be involved in the presumed greater stability of (5a) and (5b) as compared with (5c). Pyridinium ylides [*e.g.* (6)] were, however, well known but simple resonance considerations show that these have greater possibility for charge delocalisation, as indicated by the canonical forms (6a), (6b), and (6c), than analogous ammonium ylides [*e.g.* (3)], an effect that was supported by studies of acidity constants. A few simple ammonium ylides had been isolated,[7-9] but these were limited to rather special cases such as the ylides (7)—(10). More recently the highly fluorinated ylide (11) has also been described.[10]



(6a) (6b) (6c)



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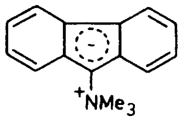
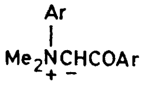


(8)

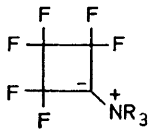
$Me_3\overset{+}{N}\overset{-}{C}(CN)_2$

(9)



$Me_2\underset{+}{N}\overset{Ar}{\underset{-}{C}}HCOAr$

(10)



(11)

The isolation of ammonium ylides analogous to (3) was therefore of interest because of our studies of the related [1,2] and [3,2] sigmatropic rearrangements of allylic ammonium ylides,[11] and the need for a mechanistic study of the 'symmetry forbidden' [1,2] rearrange-

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[†] Part 7, T. Laird, W. D. Ollis, and I. O. Sutherland, *J.C.S. Perkin 1*, 1980, 2033.

[‡] *Note added in proof.* Since this paper was submitted for publication, three relevant papers on ammonium ylides (V. Král and Z. Arnold, *Coll. Czech. Chem. Comm.*, 1980, 45, 80 and 92) and sulphonium ylides (V. Král, Z. Arnold, V. Jehlička, and O. Exner, *ibid.*, 1980, 45, 1236) have been published.

ment,[12,13] which could most conveniently be carried out using pure ylides free from metal salts.

RESULTS AND DISCUSSION

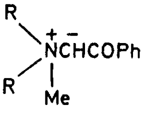
It was found that the ylide (3) could readily be prepared by treating an aqueous solution of the ammonium salt (1) at 0 °C with aqueous sodium hydroxide, and a number of analogous ylides (12a—q) and (14a—c) were prepared by similar methods from the corresponding quaternary ammonium salts (13a—q, X = Br) and (15a—c).

$R^1\overset{+}{N}Me_2\overset{-}{C}HCOR^2$
(12)

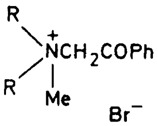
$R^1\overset{+}{N}Me_2CH_2COR^2\ X^-$
(13)

a; $R^1 = CH_2Ph$, $R^2 = p\text{-}PhC_6H_4$
b; $R^1 = CH_2Ph$, $R^2 = p\text{-}BrC_6H_4$
c; $R^1 = CH_2Ph$, $R^2 = p\text{-}O_2NC_6H_4$
d; $R^1 = p\text{-}MeC_6H_4CH_2$, $R^2 = Ph$
e; $R^1 = Me[CH_2]_9$, $R^2 = Ph$
f; $R^1 = Me[CH_2]_5CHMe$, $R^2 = Ph$
g; $R^1 = CMe_3$, $R^2 = Ph$
h; $R^1 = Me$, $R^2 = Ph$
i; $R^1 = R^2 = Ph$
j; $R^1 = Ph$, $R^2 = p\text{-}BrC_6H_4$
k; $R^1 = Ph$, $R^2 = p\text{-}O_2NC_6H_4$
l; $R^1 = Me[CH_2]_9$, $R^2 = CMe_3$
m; $R^1 = CH_2Ph$, $R^2 = CMe_3$
n; $R^1 = Me$, $R^2 = CMe_3$
p; $R^1 = p\text{-}O_2NC_6H_4CH_2$, $R^2 = Ph$
q; $R^1 = o\text{-}MeC_6H_4CH_2$, $R^2 = Ph$

The quaternary salts (13) and (15) were in all cases prepared by reacting the appropriate tertiary amine with phenacyl bromide, *p*-phenylphenacyl bromide, *p*-bromophenacyl bromide, *p*-nitrophenacyl bromide, or 3,3-dimethyl-2-oxobutyl bromide. The properties of the ylides (3), (12), and (14) are summarised in the Table and the Experimental section. In many cases the ylides were crystalline solids, but those which could readily undergo a [1,2] rearrangement were generally too unstable for recrystallisation and tended to give analytical data corresponding to hydrates. The possibility of a quaternary hydroxide structure can, however, be eliminated on a number of grounds. (*i*) The absence of a $COCH_2\overset{+}{N}$ signal in the n.m.r. spectrum and the appearance of a singlet signal assignable to $CO\overset{-}{C}H\overset{+}{N}$ (in the range τ 4.0—4.2 for phenacylanilinium ylides, τ 4.6—5.1 for phenacylammonium ylides, and τ 5.3—5.6 for 3,3-dimethylbutan-2-onylammonium ylides). This signal was generally very broad or not observable in the spectrum of a solution at 35 °C but sharpened when the solution was cooled and was easily observed for solutions at −20 °C. The broadening of the signal at higher temperatures is reminiscent of the behaviour of phosphonium ylides[14] and may well be associated with the presence of a trace of quaternary salt which undergoes a rapid *trans*-ylidation reaction with the ylide. The n.m.r. spectrum does not give any evidence for hindered rotation about the $\overset{+}{N}{-}C{=}C{-}O^-$ double bond of the enolate system (*cf*. ref. 14) but this is probably because the ylides exist exclusively in the *cis*-conformation (16) about this double bond, as found[15] in the crystal structures of the ylides (12d) and (14b). (*ii*) These crystal structures confirm the ylide structural assignment; the *cis*-conformation (16) found in the crystal structure maximises coulombic attraction between the positive and negative charges of the ylide system. This electrostatic interaction does not result in shortening of the formal $\overset{+}{N}{-}\overset{-}{C}$ bond [see alternative representations of the ylide system as in (3), (12), and (14)], found to be 1.47 Å in (12d) and 1.48 Å in (14b), similar to the normal N–C bond length; this contrasts with the situation in phosphonium[4] and sulphonium[5] ylides where multiple bonding is possible and bond shortening is observed. (*iii*) The enolate structure (16) is also consistent with the i.r. spectra of the ylides in chloroform solution (Table). The carbonyl absorption of the quaternary salts (1), (13), and (15) ($\nu_{C=O}$ 1 680—1 705 cm^{-1}) is replaced by an absorption in the range 1 540—1 570 cm^{-1}, with an



(14)



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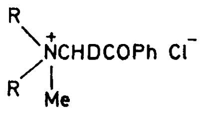
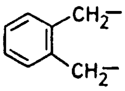


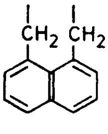
(17)

a; R,R = $-[CH_2]_4-$,

b; R,R =



c; R,R =

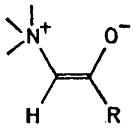


Properties of ammonium ylides (3), (12), and (14)

Compound	Solvent for preparation	M.p./°C	τ ($\overset{-}{C}H$)[a]	$\nu_{max.}$/cm^{-1}
(3)	H_2O	70—71[b]	4.98	1 590, 1 550
(12a)	H_2O	50—51	4.98	1 590, 1 570
(12b)	H_2O–MeOH (7.5 : 1)	52—53	5.00	1 585, 1 540
(12c)	H_2O–MeOH (9 : 1)	46	4.89	1 565
(12d)	H_2O	66—67[b]	5.10	1 585, 1 550
(12e)	H_2O	66[d,e]	4.83	1 585, 1 550
(12f)	H_2O	54—55[b,e]	4.75	1 595, 1 555
(12g)	CH_2Cl_2	Unstable	4.74	1 595, 1 555
(12h)	H_2O	*c*	4.65	1 585, 1 545
(12i)	H_2O[f]	gum	4.16	1 580, 1 540
(12j)	H_2O	117—118	4.26	1 580, 1 540
(12k)	H_2O–MeOH (1 : 2)	93—94	4.02	1 555
(12l)	H_2O	30—32[e]	5.39	1 555
(12m)	H_2O	60	5.56	1 550
(12n)	H_2O	171—172	*g*	1 550
(14a)	H_2O[f]	*c*	4.76	1 585, 1 545
(14b)	H_2O[f]	156—157[d,e]	*g*	1 575, 1 530
(14c)	H_2O[f]	165[d,e]	*g*	1 590, 1 550

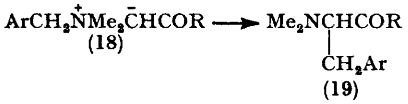
[a] This signal generally not observable in the n.m.r. spectra run at 35 °C; the data refer to spectra run at −20 °C. [b] Elemental analysis indicates that the crystals are hydrated. [c] These ylides were obtained as hygroscopic solids, melting points poorly defined. [d] Elemental analysis consistent with an anhydrous ylide. [e] These ylides could be purified by recrystallisation. [f] Isolated by extraction with CH_2Cl_2 or $CHCl_3$. [g] Spectrum not run at −20 °C.

additional strong band in the region 1 580—1 595 cm^{-1} for ylides having an aromatic ring in their structure. This change in the i.r. spectrum has proved to be an excellent way of distinguishing carbonyl-stabilised ammonium ylides from the corresponding quaternary salts. (*iv*) A few ylides could be purified by recrystallisation and the molecular formula could then be established by elemental analysis, and in general the molecular formula required for the ylide was consistent with the value of *m*/*e* found for the molecular ion in the mass spectrum. (*v*) The quaternary salts (1), (13), and (15) could be regenerated from the ylides (3), (12), and (14) by treatment with hydrobromic acid, but on treatment with deuterium chloride the ylides (14b) and (14c) gave the monodeuteriated quaternary salts (17b) and (17c), respectively [COC*H*D$\overset{+}{\mathrm{N}}$ as a 1 H singlet in the n.m.r. spectrum; (17b) at τ 4.48 and (17c) at τ 4.92].



(16)

The phenacylammonium ylides are usually thermally unstable with respect to either Stevens [1,2] rearrangement or fragmentation to give the parent tertiary amine and products formally derived from a PhCOCH: fragment. Thus the ylides (18) [(3), (12a), (12b), (12c), (12d), and (12m)] having an $\overset{+}{\mathrm{N}}$-benzyl substituent, rearranged cleanly on heating at 53 °C to give good yields of the [1,2] rearrangement products (19). The rate of rearrangement of the ylides (18) depends upon the nature of the substituent Ar; in the cases of the ylides (12p ≡ 18; Ar = p-$C_6H_4NO_2$, R = Ph) and (12q ≡ 18; Ar = o-C_6H_4Me, R = Ph) the rearrangement occurred too rapidly, even at 0 °C, to permit isolation of the ylide and attempted ylide preparation gave largely the rearrangement products (19f) and (19g).

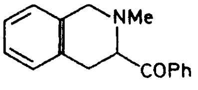


$$\underset{(18)}{\mathrm{ArCH_2\overset{+}{N}Me_2\overset{-}{C}HCOR}} \longrightarrow \mathrm{Me_2N\underset{\substack{|\\ \mathrm{CH_2Ar}\\ (19)}}{C}HCOR}$$

	R	Ar
a;	p-$C_6H_4C_6H_5$	Ph
b;	p-C_6H_4Br	Ph
c;	p-$C_6H_4NO_2$	Ph
d;	Ph	p-C_6H_4Me
e;	CMe_3	Ph
f;	Ph	p-$C_6H_4NO_2$
g;	Ph	o-C_6H_4Me

Surprisingly, the ylides (14b) and (14c), which have structures analogous to those of the ylides (18), were thermally rather stable. Thus the isoindolinium ylide (14b) rearranged only on heating at 150 °C to give a good yield of the expected keto-amine (20), but the ylide (14c) failed to rearrange, and underwent fragmentation at its melting point to give the tertiary amine (21) and *trans*-1,2,3-tribenzoylcyclopropane (22), formally derivable by trimerisation of the carbene PhCOCH:. The failure of the ylides (14b) and (14c) to rearrange readily can be accounted for in the terms of steric hindrance to the attainment of a geometry suitable for full resonance-stabilisation of the benzylic radical centre in the diradicals (23) and (24), required as intermediates for the [1,2] rearrangement.*

In accord with this view, thermolysis of the decyldimethylammonium ylide (12e) at 150 °C gave the cyclopropane (22), *trans*-1,2-dibenzoylethylene (25), and the cyclopentapyran (26), all three products formally derivable from the carbene PhCOCH:, together with decyldimethylamine. Similar reactions have been observed from trimethylammonium phenacylides [16] and products formally derivable from carbenes are commonly observed in other reactions of ammonium ylides (see below) and sulphonium ylides.[7,17] It is of interest that the cyclopropane (22) and the cyclopentapyran (26) are also formed by the reaction of *trans*-1,2-dibenzoylethylene (25) with the ylide (3) at 0 °C.



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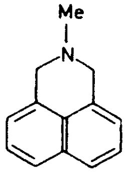

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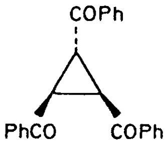

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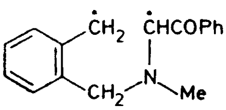

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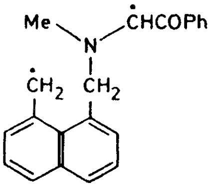

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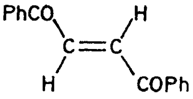

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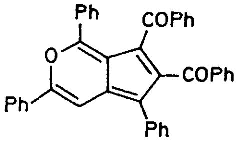

(26)

The products of competing Hofmann elimination or [1,2] rearrangement were not detectable in the case of the ylide (12e) but, in contrast, the t-butyldimethylammonium ylide (12g) decomposes rapidly above room temperature and gives *NN*-dimethyl phenacylamine together with, presumably, 2-methylpropene. It may be noted that Hofmann elimination involving an ammonium ylide as an intermediate is a rare event, and in the case of the ylide (12g) it may involve the corresponding

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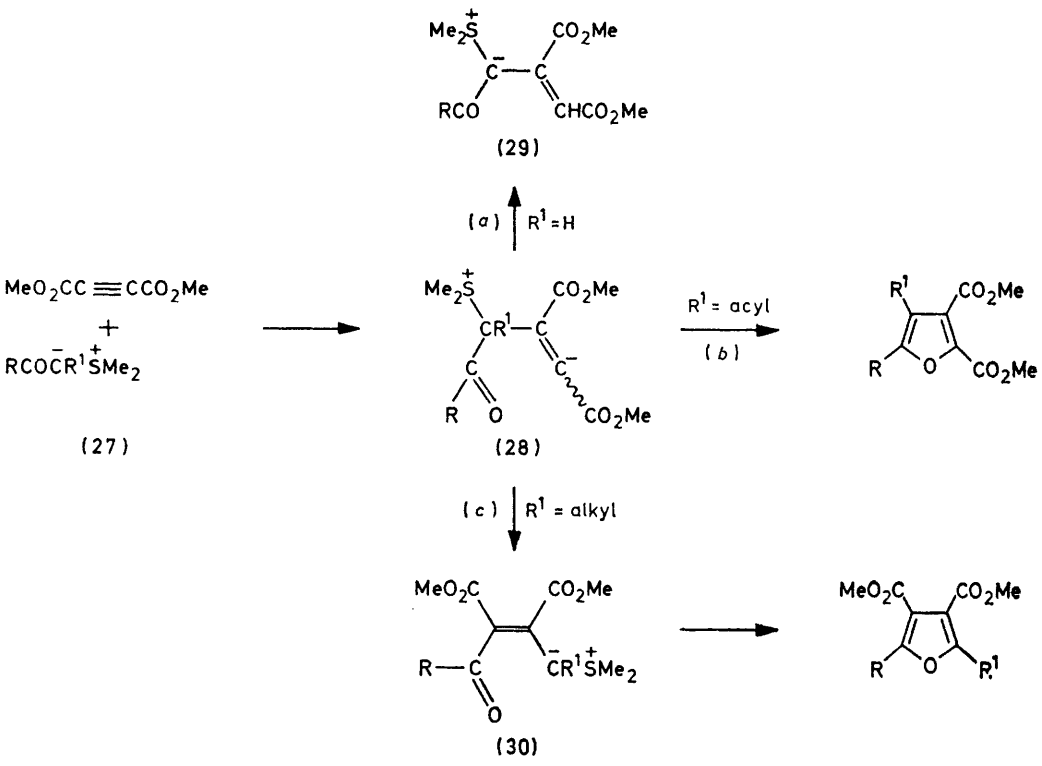
* Evidence for the involvement of radical intermediates in the Stevens [1,2]rearrangement will be presented in a future paper of this series (*cf.* ref. 13).

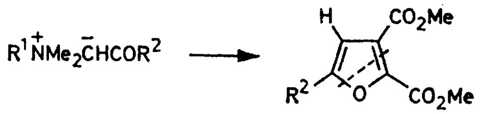
quaternary ammonium hydroxide if the ylide contains traces of moisture.

Sulphonium ylides (27) have been reported to react in three different ways with acetylene dicarboxylic acid esters [18-20] (see Scheme 1). Thus addition of the carbanion centre of the ylide to the triple bond gives an intermediate betaine (28), which can undergo a formal [1,3] hydrogen migration [18] to give an ylide (29) [pathway (*a*), $R^1 = H$], cyclisation with loss of dimethyl sulphide to give [19] a furan derivative [pathway (*b*), R^1 = acyl], or a formal [1,3] acyl migration [20] to give an ylide (30) followed by cyclisation and loss of dimethyl sulphide to give a different furan derivative [pathway (*c*), R^1 = alkyl].



Scheme 1

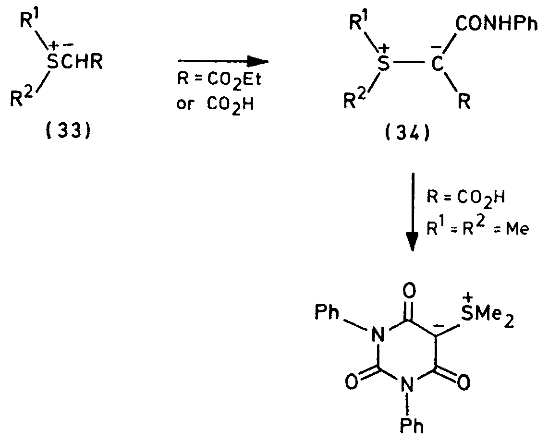
The ammonium ylides (31) [(3), (12a), (12b), (12c), and (12m)] react with dimethyl acetylenedicarboxylate in a manner analogous to pathway (*b*) (Scheme 1) to give moderate yields of the furan derivatives (32). The products (32) were characterised by their spectroscopic properties [$\nu_{C=O}$ 1 725—1 740 cm^{-1}; n.m.r. singlet in the range τ 2.00—2.23 (furan 4-H)] and their mass-spectral fragmentation which in each case gave a fragment ion corresponding to the loss of 87 a.m.u. ($COCO_2Me$) consistent with the expected cleavage indicated by the broken line in (32). The ylides (14b) and (14c) reacted in a similar manner with dimethyl acetylenedicarboxylate to give the furan (32a), together with the corresponding tertiary amine.



(31) (32)

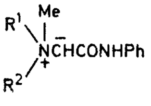
R^2
a ; Ph
b ; p-C_6H_4Ph
c ; p-C_6H_4Br
d ; p-$C_6H_4NO_2$
e ; CMe_3

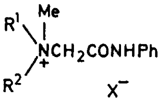
Sulphonium ylides (33) have been reported to react with phenyl isocyanate [21] to give new ylides (34) in which hydrogen atoms adjacent to the carbanion centre have been replaced by phenylcarbamoyl groups (Scheme 2). In certain cases the carbamoyl ylides (34) can react further to give pyrimidine derivatives.[22b] Similar reactions have been reported [22] for pyridinium ylides. The ylides (14b) and (14c) each reacted with an excess of phenyl isocyanate to give the new ylides (35a) and (35b), respectively. The ylides (35) were identified on the basis of their molecular formulae and spectroscopic properties [(35a) only], and by the generation of the quaternary salts (36) on treatment with either hydrogen chloride (36b; X = Cl) or toluene-*p*-sulphonic acid (36a; X = p-$MeC_6H_4SO_3$). The ylides (35) could be regenerated by reaction of the salts (36) with base. The other product of the reaction between the ylides

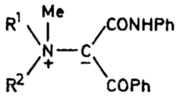


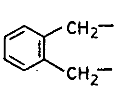
SCHEME 2

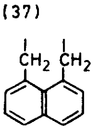
(14b) and (14c) with phenyl isocyanate was benzanilide, presumably formed, together with (35), by the reaction of the expected reaction product (37) (*cf.* Scheme 2) with aniline produced by partial hydrolysis of phenyl isocyanate [the ylides (14) are hygroscopic]. The reaction of the ylide (3) with phenyl isocyanate proceeded a stage further and the presumed intermediate ylide (35; $R^1 = Me$, $R^2 = CH_2Ph$) reacted with further phenyl isocyanate to give the pyrimidine derivative (38) (*cf.* Scheme 2), together with aniline, *NN*-diphenylurea, and benzanilide. The structure of the ylide (38) is consistent with its molecular formula and spectroscopic properties (i.r. and n.m.r. spectra), reaction with hydrobromic acid which gives the corresponding quaternary salt (39), and thermal rearrangement at 200 °C to give the product (40) of a [1,2] rearrangement.

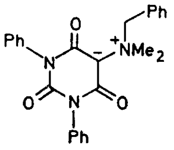

(35)


(36)


(37)

a ; R^1,R^2 =


b ; R^1,R^2 =
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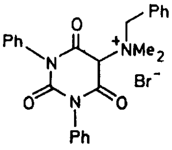
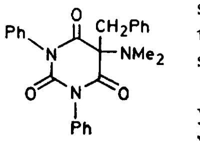
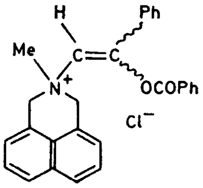
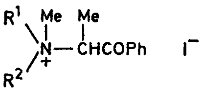
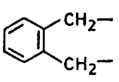

(39)

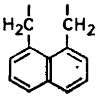

(40)


(42)


(41)

a ; R^1 = Me , R^2 = CH_2Ph

b ; R^1,R^2 =


c ; R^1,R^2 =


Alkylation and acylation of the carbanionic centres of the ammonium ylides (3), (12), and (14) were rather disappointing, and only positive results are reported here. Thus the reaction of the ylides (3) and (14b and c) with methyl iodide gave mixtures of the expected *C*-methylated quaternary salts (41) together with quaternary iodides (1; I^- rather than Br^-) and (15b and c; I^- rather than Br^-) resulting from addition of hydrogen iodide. The ylide (14c) reacted with benzoyl chloride to give a good yield of the expected quaternary enol benzoate (42).

The relatively few reactions, other than sigmatropic rearrangement, of the acylammonium ylides (3), (12), and (14), discussed in this paper contrast with the rich chemistry of sulphonium [7,17] and phosphonium ylides [7,23] suggesting that further investigation might be profitable. The best analogy of the reactivity of the ammonium ylides is that of the sulphonium ylides in that in both cases [1,2] or [3,2] rearrangements occur readily when a suitable migrating group is attached to the onium centre and a number of other reactions are formally alkylidene transfer reactions.

EXPERIMENTAL

The general directions are given in Part 1.[11a]

Quaternary Ammonium Salts (1), (13), *and* (15).—The following procedure is typical. The tertiary amine (0.1 mol) was added dropwise to a stirred solution of the halide (0.1 mol) in methyl cyanide (100—250 ml). The resulting solution was heated on a steam-bath for 15 min and allowed to stand at room temperature for 3 h. The precipitated salt was recrystallised from methanol–ether. The properties and characterisation of the quaternary ammonium salts (1), (13), and (15) are listed below.

Benzyldimethyl(phenacyl)ammonium bromide (1) (87% yield) had m.p. 166—167 °C (lit.,[1] m.p. 167—168 °C); $\nu_{max.}$ 1 690 cm^{-1}; $\tau(CDCl_3)$ 1.99 (dd, *J* 8, 2 Hz, 2 *ortho*-H of PhCO), 2.33—2.69 (m, 8 aryl-H), 4.20 (s, $COCH_2\overset{+}{N}$), 4.67 (s, $\overset{+}{N}CH_2Ph$), and 6.46 (s, $\overset{+}{N}Me_2$).

Benzyldimethyl-(*p*-phenylphenacyl)ammonium bromide (13a; X = Br) (81% yield) had m.p. 205 °C (lit.,[24] m.p. 207 °C) (Found: C, 67.0; H, 5.8; N, 3.3; Br, 19.4. Calc. for $C_{23}H_{24}BrNO$: C, 67.3; H, 5.9; N, 3.4; Br, 19.5%); $\nu_{max.}$ (KBr) 1 685 cm^{-1}; $\tau(CF_3CO_2H)$, τ_A 1.95, τ_B 2.24 (AA′BB′ system, J_{AB} 8.5 Hz, *p*-PhC_6H_4), 2.34—2.61 (m, 10 aryl-H), 4.97 (s, $COCH_2\overset{+}{N}$), 5.05 (s, $\overset{+}{N}CH_2Ph$), and 6.53 (s, $\overset{+}{N}Me_2$).

Benzyl-(*p*-bromophenacyl)dimethylammonium bromide (13b; X = Br) (87% yield) had m.p. 187 °C (lit.,[2] 187—191 °C) (Found: C, 49.5; H, 4.6; N, 3.1; Br, 38.9. Calc. for $C_{17}H_{19}Br_2NO$: C, 49.5; H, 4.4; N, 3.4; Br, 38.8%); $\nu_{max.}$ (KBr) 1 690 cm^{-1}; $\tau(CF_3CO_2H)$, τ_A 2.12, τ_B 2.32 (AA′BB′ system, J_{AB} 9 Hz, *p*-BrC_6H_4), 2.39—2.60 (m, 5 aryl-H), 4.96 (s, $COCH_2\overset{+}{N}$), 5.20 (s, $\overset{+}{N}CH_2Ph$), and 6.52 (s, $\overset{+}{N}Me_2$).

Benzyldimethyl-(p-*nitrophenacyl*)*ammonium bromide* (13c; X = Br) (90% yield) had m.p. 184 °C (Found: C, 54.1; H, 5.1; N, 7.2; Br, 21.2. $C_{17}H_{19}Br\,N_2O_3$ requires C, 53.8; H, 5.05; N, 7.4; Br, 21.1%); $\nu_{max.}$ (KBr) 1 700 cm^{-1}; $\tau(CF_3CO_2H)$, τ_A 1.60, τ_B 1.74 (AA′BB′ system, J_{AB} 8 Hz, p-$O_2NC_6H_4$), 2.46 (s, 5 aryl-H), 4.82 (s, $COCH_2\overset{+}{N}$), 5.00 (s, $PhCH_2\overset{+}{N}$), and 6.48 (s, $\overset{+}{N}Me_2$).

Dimethyl-(p-*methylbenzyl*)*phenacylammonium bromide* (13d; X = Br) (80% yield) had m.p. 175 °C (Found: C, 61.7; H, 6.4; N, 3.7; Br, 23.1. $C_{18}H_{22}BrNO$ requires C, 62.1; H, 6.4; N, 4.0; Br, 22.9%); $\nu_{max.}$ (KBr) 1 690 cm^{-1}; $\tau(CF_3CO_2H)$, 2.03 (dd, J 8, 2 Hz, 2 *ortho*-H of PhCO), 2.21—2.59 (m, 3 aryl-H), 2.68 (s, p-MeC_6H_4), 5.00 (s, $COCH_2\overset{+}{N}$), 5.09 (s, $\overset{+}{N}CH_2Ar$), 6.54 (s, $\overset{+}{N}Me_2$), and 7.62 (s, Ar-Me).

Decyldimethylphenacylammonium bromide (13e; X = Br) (87% yield) had m.p. 112—113 °C (Found: C, 63.7; H, 8.7; N, 3.35; Br, 20.7. $C_{20}H_{34}BrNO$ requires C, 62.5; H, 8.9; N, 3.65; Br, 20.8%); $\nu_{max.}$ 1 690 cm^{-1}; $\tau(CF_3CO_2H)$, 2.00 (dd, J 8, 2 Hz, 2 *ortho*-H of PhCO), 2.19—2.55 (m, 3 aryl-H), 4.88 (s, $COCH_2\overset{+}{N}$), 6.13—6.30 (m, $\overset{+}{N}CH_2C_9H_{19}$), 6.52 (s, $\overset{+}{N}Me_2$), 7.95—8.34 (m, $\overset{+}{N}CH_2CH_2C_8H_{17}$), 8.62 (br m, $\overset{+}{N}CH_2CH_2C_7H_{14}Me$), and 9.12 (m, CH_2Me).

Dimethyl-(2-*octyl*)*phenacylammonium bromide* (13f; X = Br) (89% yield) had m.p. 138 °C (Found: C, 60.4; H, 8.4; N, 3.9; Br, 22.7. $C_{18}H_{30}BrNO$ requires C, 60.7; H, 8.4; N, 3.9; Br, 22.5%); $\nu_{max.}$ 1 695 cm^{-1}; τ 1.82 (d, J 8 Hz, 2 *ortho*-H of PhCO), 2.34—2.66 (m, 3 aryl-H), 4.07 (s, $COCH_2\overset{+}{N}$), 5.53—5.82 (m, $\overset{+}{N}CH$), 6.41 (s, $\overset{+}{N}Me_2$), 7.89—9.00 (m, $\overset{+}{N}CHMe + \overset{+}{N}CHC_5H_{10}Me$), and 9.16 (m, CH_2Me).

t-Butyldimethyl(*phenacyl*)*ammonium bromide* (13g; X = Br) (88% yield) had m.p. 129—130 °C (Found: C, 55.9; H, 7.3; N, 4.6; Br, 26.65. $C_{14}H_{22}BrNO$ requires C, 56.0; H, 7.4; N, 4.7; Br, 26.7%); $\nu_{max.}$ 1 690 cm^{-1}; τ 2.07 (d, J 8 Hz, 2 *ortho*-H of PhCO), 2.30—2.59 (m, 3 aryl-H), 5.03 (s, $COCH_2\overset{+}{N}$), 6.57 (s, $\overset{+}{N}Me_2$), and 8.31 (s, CMe_3).

NN-*Dimethyl-*N-*phenacylanilinium bromide* (13i; X = Br) (76% yield) had m.p. 118—119 °C (Found: C, 59.7; H, 5.6; N, 4.2; Br, 25.1. $C_{16}H_{18}BrNO$ requires C, 60.0; H, 5.7; N, 4.4; Br, 24.95%); $\nu_{max.}$ 1 695 cm^{-1}; $\tau(CF_3CO_2H)$, 2.02—2.63 (m, 10 aryl-H), 4.10 (s, $COCH_2\overset{+}{N}$), and 6.03 (s, $\overset{+}{N}Me_2$).

N-(*p*-Bromophenacyl)-*NN*-dimethylanilinium bromide (13j; X = Br) (67% yield) had m.p. 152 °C (lit.,[25] m.p. 153 °C); $\nu_{max.}$ (KBr) 1 695 cm^{-1}; $\tau(CF_3CO_2H)$, 2.14—2.46 (m, 9 aryl-H), 4.18 (s, $COCH_2\overset{+}{N}$), and 6.04 (s, $\overset{+}{N}Me_2$).

NN-Dimethyl-*N*-(*p*-nitrophenacyl)anilinium bromide (13k; X = Br) (82% yield) had m.p. 121—122 °C (lit.,[26] m.p. 122—123 °C) (Found: C, 50.0; H, 5.0; N, 7.3; Br, 20.8. Calc. for $C_{16}H_{17}BrN_2O_3{\cdot}H_2O$: C, 50.2; H, 5.0; N, 7.3; Br, 20.9%); $\nu_{max.}$ (KBr) 1 695 cm^{-1}; $\tau(CF_3CO_2H)$, τ_A 1.64, τ_B 1.80 (AA′BB′ system, J_{AB} 8.5 Hz, p-$O_2NC_6H_4$), 2.07—2.43 (m, 5 aryl-H), 4.00 (s, $COCH_2\overset{+}{N}$), and 5.96 (s, $\overset{+}{N}Me_2$). The above salt was prepared using the two reactants in methyl cyanide at room temperature; if the solution was heated the resulting salt was accompanied by N-*methyl-*N-(p-*nitrophenacyl*)*aniline* (Found: C, 66.6; H, 5.3; N, 10.4. $C_{15}H_{14}N_2O_3$ requires C, 66.7; H, 5.2; N, 10.4%); $\nu_{max.}$ 1 700 cm^{-1}; τ, τ_A 1.75, τ_B 1.95 (AA′BB′ system, J_{AB} 9 Hz, p-$O_2NC_6H_4$), 2.76—3.40 (m, 5 aryl-H), 5.29 (s, $COCH_2N$), and 6.95 (s, NMe).

Decyldimethyl-(3,3-*dimethyl-*2-*oxobutyl*)*ammonium bromide* (13l; X = Br) (87% yield) had m.p. 110 °C (from methyl cyanide–ether) (Found: C, 59.7; H, 10.6; N, 3.6; Br, 21.9. $C_{18}H_{38}BrNO$ requires C, 59.3; H, 10.4; N, 3.85; Br, 22.0%); $\nu_{max.}$ 1 705 cm^{-1}; τ 4.58 (s, $COCH_2\overset{+}{N}$), 6.04—6.36 (br m, $\overset{+}{N}CH_2C_9H_{19}$), 6.45 (s, $\overset{+}{N}Me_2$), 8.07—8.47 (br m, $\overset{+}{N}CH_2CH_2C_8H_{17}$), 8.73 (br s, $CMe_3 + \overset{+}{N}CH_2CH_2[CH_2]_7Me$), and 9.07—9.19 (m, $\overset{+}{N}[CH_2]_9Me$).

Benzyldimethyl-(3,3-*dimethyl-*2-*oxobutyl*)*ammonium bromide* (13m; X = Br) (83% yield) was obtained as a gum (Found: C, 57.0; H, 7.5; N, 4.3; Br, 25.2. $C_{15}H_{24}BrNO$ requires C, 57.3; H, 7.7; N, 4.5; Br, 25.4%); $\nu_{max.}$ 1 705 cm^{-1}; τ 2.25—2.58 (m, 5 aryl-H), 4.63 (s, $COCH_2\overset{+}{N}$), 4.72 (s, $\overset{+}{N}CH_2Ph$), 6.50 (s, $\overset{+}{N}Me_2$), and 8.74 (s, CMe_3).

Trimethyl-(3,3-*dimethyl-*2-*oxobutyl*)*ammonium bromide* (13n; X = Br) was prepared from trimethylamine and 1-bromo-3,3-dimethylbutan-2-one in ethanol at room temperature for 2 h. The *salt* (76% yield) had m.p. 259—260 °C (Found: C, 45.5; H, 8.3; N, 6.2; Br, 33.6. $C_9H_{20}BrNO$ requires C, 45.5; H, 8.5; N, 5.9; Br, 33.55%); $\nu_{max.}$ 1 705 cm^{-1}; $\tau(CF_3CO_2H)$, 5.30 (s, $COCH_2\overset{+}{N}$), 6.55 (s, $\overset{+}{N}Me_3$), and 8.71 (s, CMe_3).

Dimethyl-[(*p*-nitrobenzyl)phenacyl]ammonium bromide (13p; X = Br) (80% yield) had m.p. 166—167 °C (lit.,[27] 169—171 °C) (Found: C, 53.7; H, 4.8; N, 7.3; Br, 20.75. Calc. for $C_{17}H_{19}BrN_2O_3$: C, 53.8; H, 5.05; N, 7.4; Br 21.1%); $\nu_{max.}$ (KBr) 1 680 cm^{-1}; $\tau(CF_3CO_2H)$, AA′BB′ system, τ_A 1.62, τ_B 2.12 (J_{AB} 8.5 Hz, p-$O_2NC_6H_4$), 1.95 (d, J 7.5 Hz, 2 *ortho*-H of C_6H_5CO), 2.20—2.50 (m, 3 aryl-H), 4.78 (s, $COCH_2\overset{+}{N} + ArCH_2\overset{+}{N}$), and 6.40 (s, $\overset{+}{N}Me_2$).

Dimethyl-[(*o*-methylbenzyl)phenacyl]ammonium bromide (13q; X = Br) (80% yield) had m.p. 136—137 °C (lit.,[27] gum); $\nu_{max.}$ 1 685 cm^{-1}; τ 2.00 (d, 2 *ortho*-H of C_6H_5CO), 2.43—2.76 (m, 7 aryl-H), 3.94 (s, $COCH_2\overset{+}{N}$), 4.77 (s, $\overset{+}{N}CH_2Ar$), 6.58 (s, $\overset{+}{N}Me_2$), and 7.51 (s, Ar–Me).

N-*Methyl-*N-*phenacylpyrrolidinium bromide* (15a) (88% yield) had m.p. 169—170 °C (Found: C, 55.2; H, 6.5; N, 4.9; Br, 28.25. $C_{13}H_{18}BrNO$ requires C, 54.9; H, 6.3; N, 4.9; Br, 28.2%); $\nu_{max.}$ 1 685 cm^{-1}; $\tau(CF_3CO_2H)$, 1.94 (dd, J 8, 2 Hz, 2 *ortho*-H of PhCO), 2.20—2.57 (m, 3 aryl-H), 4.67 (s, $COCH_2\overset{+}{N}$), 5.80—6.18 (m, $CH_2\overset{+}{N}CH_2$), 6.50 (s, $\overset{+}{N}Me$), and 7.40—7.70 (m, CH_2CH_2).

2-Methyl-2-phenacylisoindolinium chloride (15b; Cl^- in place of Br^-) (with A. J. Pretty) (94% yield) had m.p. 207—208 °C (Found: C, 70.1; H, 6.1; N, 4.9; Cl, 12.1. Calc. for $C_{17}H_{18}ClNO$: C, 70.9; H, 6.3; N, 4.9; Cl, 12.3%); $\nu_{max.}$ 1 680 cm^{-1}; $\tau(CF_3CO_2H)$ 1.94—2.50 (m, 9 aryl-H), 4.47 (s, $\overset{+}{N}CH_2CO$), 4.77 (s, 2 × $ArCH_2$), and 6.42 (s, $\overset{+}{N}Me$).

2-*Methyl-*2-*phenacyl-*2,3-*dihydro-*1H-*benz*[de]*isoquinolinium bromide* (15c) (with S. E. Potter) (91% yield) had m.p. 165 °C (Found: C, 65.8; H, 5.1; N, 3.5; Br, 21.1. $C_{21}H_{20}BrNO$ requires C, 66.0; H, 5.2; N, 3.7; Br, 20.9%);

$\nu_{max.}$ 1 680 cm^{-1}; τ(CF_3CO_2H) 1.85—2.69 (m, 11 aryl-H), AB system, τ_A 4.38, τ_B 4.77 (J_{AB} 15 Hz, 2 × $\overset{+}{N}CH_AH_BAr$), 4.74 (s, $\overset{+}{N}CH_2CO$), and 6.24 (s, $\overset{+}{N}Me$).

Ylides (3), (12), *and* (14).—The following procedure is typical. Cold (0 °C) aqueous sodium hydroxide (10—15%, 100 ml) was added to a solution of the quaternary ammonium salt (1), (13), or (15) (*ca.* 0.1 mol) in water at 0 °C. The mixture was stored at 0 °C for a further 4 h and the precipitated ylide removed by filtration, washed with water and ether, and dried *in vacuo*. The properties and characterisation of the ylides (3), (12), and (14) are listed below.

Anhydro[benzyldimethyl(phenacyl)ammonium hydroxide] (3) (91% yield) had m.p. 70—71 °C [Found: C, 75.7; H, 7.5; N, 5.2%; *M*, 253.* $C_{17}H_{19}NO{\cdot}H_2O$ requires C, 75.3; H, 7.8; N, 5.2%; *M* ($C_{17}H_{19}NO$), 253]; τ (−20 °C) 2.26—2.74 (m, 10 aryl-H), 4.98 (s, $\overset{+}{N}CH_2Ph$ + $CO\overset{-}{C}H\overset{+}{N}$), and 6.75 (s, $\overset{+}{N}Me_2$).

Anhydro[benzyldimethyl-(p-*phenylphenacyl)ammonium hydroxide]* (12a) (83% yield) was obtained as colourless plates, m.p. 50—51 °C (Found: M^+, 329. $C_{23}H_{23}NO$ requires *M*, 329); τ (−20 °C) 2.22—2.74 (m, 14 aryl-H), 4.98 (s, $\overset{+}{N}CH_2Ph$ + $CO\overset{-}{C}H\overset{+}{N}$), and 6.77 (s, $\overset{+}{N}Me_2$).

Anhydro[benzyl-(p-*bromophenacyl)dimethylammonium hydroxide]* (12b) (84% yield) was prepared using a solution of the ammonium salt (15 g) in water (1 500 ml) containing methanol (200 ml). The *ylide* (12b) had m.p. 52—53 °C (Found: M^+, 332. $C_{17}H_{18}BrNO$ requires *M*, 332); τ (−20 °C) 2.43—2.63 (m, 9 aryl-H), 5.00 (s, $\overset{+}{N}CH_2Ph$ + $CO\overset{-}{C}H\overset{+}{N}$), and 6.75 (s, $\overset{+}{N}Me_2$).

Anhydro[benzyldimethyl-(p-*nitrophenacyl)ammonium hydroxide]* (12c) (71% yield) was prepared using a solution of the ammonium salt (10 g) in water (1 350 ml) containing methanol (150 ml). The ylide (12c) was obtained as yellow needles, m.p. 46 °C (Found: M^+, 298. $C_{17}H_{18}N_2O_3$ requires *M*, 298); τ (−20 °C), AA′BB′ system, τ_A 1.83, τ_B 2.16 (J_{AB}, $J_{A'B'}$ 8 Hz, *p*-$COC_6H_4NO_2$), 2.61 (s, Ph), 4.89 (s, $CO\overset{-}{C}H\overset{+}{N}$), 4.95 (s, $\overset{+}{N}CH_2Ph$), and 6.68 (s, $\overset{+}{N}Me_2$).

Anhydro[dimethyl-(p-*methylbenzyl)phenacylammonium hydroxide]* (12d) (65% yield) was obtained as pale yellow plates, m.p. 66—67 °C [Found: C, 76.2; H, 8.1; N, 4.7%; M^+, 267. $C_{18}H_{21}NO{\cdot}H_2O$ requires C, 75.8; H, 8.1; N, 4.9%; *M* ($C_{18}H_{21}NO$), 267]; τ (−20 °C) 2.28—3.00 (m, 9 aryl-H), 5.10 (s, $\overset{+}{N}CH_2Ar$ + $CO\overset{-}{C}H\overset{+}{N}$), 6.83 (s, $\overset{+}{N}Me_2$), and 7.70 (s, Ar-*Me*).

Anhydro[decyldimethyl(phenacyl)ammonium hydroxide] (12e) (88% yield) was obtained as colourless plates, m.p. 66 °C, by crystallisation from tetrahydrofuran–light petroleum (Found: C, 79.2; H, 11.2; N, 4.5%; M^+, 303. 256 7. $C_{20}H_{33}NO$ requires C, 79.2; H, 11.0; N, 4.6%; *M*, 303.256 2); τ (−20 °C) 2.30—2.80 (m, Ph), 4.83 (s, $CO\overset{-}{C}H\overset{+}{N}$), 6.30—6.54 (m, $\overset{+}{N}CH_2$), 6.72 (s, $\overset{+}{N}Me_2$), 8.20—8.56 (m, $\overset{+}{N}CH_2CH_2$), 8.77 (br m, $[CH_2]_7$), and 9.17 (br t, CH_2Me).

Anhydro[dimethyl-(1-methylheptyl)phenacylammonium hydroxide] (12f) (*ca.* 100% yield) was obtained as long colourless needles, m.p. 54—55 °C, by crystallisation from ether–light petroleum [Found: C, 69.11; H, 10.2; N, 4.3%; M^+, 257.224 2. $C_{18}H_{29}NO{\cdot}2H_2O$ requires C, 69.4; H, 10.6; N, 4.5%; *M* ($C_{18}H_{29}NO$), 257.224 7]; τ (−20 °C) 2.25—2.77 (m, Ph), 4.75 (s, $CO\overset{-}{C}H\overset{+}{N}$), 5.29—5.77 (m, $NCHC_6H_{13}$), 6.69 (s, $\overset{+}{N}Me$), 6.77 (s, $\overset{+}{N}Me$), 7.76—8.80 [m, $\overset{+}{N}CH(Me)C_5H_{10}$], and 9.13 (br t, CH_2Me).

Anhydro-[t-butyldimethyl(phenacyl)ammonium hydroxide] (12g) (45% yield) was obtained as unstable microcrystals by precipitation with light petroleum from a solution in methylene chloride; τ (−20 °C) 2.27—2.37 (m, 2 *ortho*-H of PhCO), 2.65—2.78 (m, 3 aryl-H), 4.74 (s, $CO\overset{-}{C}H\overset{+}{N}$), 6.47 (s, $\overset{+}{N}Me_2$), and 8.47 (s, CMe_3).

Anhydro[trimethyl(phenacyl)ammonium hydroxide] (12h). This ylide is soluble in water and a different method of preparation was used. The ammonium salt (13h; X = Br) (10 g) in water (250 ml) was shaken with an excess of silver oxide for 2 h at room temperature. The mixture was stored at 0 °C for 12 h, silver salts removed by filtration, and the filtrate evaporated under reduced pressure at 25 °C. The residual gum was extracted with ether leaving the ylide (12h) (5 g) as a hygroscopic solid (Found: M^+, 177.115 6. $C_{11}H_{15}NO$ requires *M*, 177.115 4); τ 2.33—2.43 (m, 2 *ortho*-H of PhCO), 2.57—2.90 (m, 3 aryl-H), 4.65 (br s, $CO\overset{-}{C}H\overset{+}{N}$), and 6.65 (s, $\overset{+}{N}Me_3$). The ylide could also be obtained as a hygroscopic solid (60% yield) using aqueous sodium hydroxide (10 ml, 50%) and the ammonium salt (13h; X = Br) (5 g) in water (15 ml).

Anhydro-(NN-*dimethyl-*N-*phenacylanilinium hydroxide*) (12i) was extracted from an aqueous solution into methylene chloride. The extract was evaporated and the residue shaken with dry ether to leave the ylide (12i) (80% yield) as a gum (Found: M^+, 239.130 6. $C_{16}H_{17}NO$ requires *M*, 239.131 0); τ (−20 °C) 2.23—2.31 (m, 2 *ortho*-H of PhCO), 2.60—2.78 (m, 8 aryl-H), 4.16 (s, $CO\overset{-}{C}H\overset{+}{N}$), and 6.25 (s, $\overset{+}{N}Me_2$).

Anhydro-[*NN*-dimethyl-*N*-(p-bromophenacyl)anilinium hydroxide] (12j) was obtained (87% yield) as colourless plates, m.p. 117—118 °C (lit.,[26] 119 °C) (Found: M^+, 318. Calc. for $C_{16}H_{16}BrNO$: *M*, 318); τ 2.20—2.70 (m, 9 aryl-H), 4.26 (s, $CO\overset{-}{C}H\overset{+}{N}$), and 6.20 (s, $\overset{+}{N}Me_2$).

*Anhydro-[*NN-*dimethyl-*N-*(*p-*bromophenacyl)anilinium hydroxide]* (12k) (48% yield) was prepared using a solution of the ammonium salt (10 g) in methanol (200 ml) and water (100 ml) and aqueous sodium hydroxide (25 ml, 40%). The ylide (12k) was obtained as yellow plates, m.p. 93—94 °C (Found: M^+, 284.115 1. $C_{16}H_{16}N_2O_3$ requires M^+, 284.116 1); τ(−20 °C) AA′BB′ system, τ_A 1.88, τ_B 2.15 (J_{AB}, $J_{A'B'}$ 9 Hz, *p*-$O_2NC_6H_4$), 2.42—2.56 (m, Ph), 4.02 (s, $CO\overset{-}{C}H\overset{+}{N}$), and 6.09 (s, $\overset{+}{N}Me_2$).

Anhydro[decyldimethyl-(3,3-dimethyl-2-oxobutyl)ammonium hydroxide] (12l) was obtained (52% yield) as colourless plates, m.p. 30—32 °C after crystallisation from ether–light petroleum (Found: M^+, 283.287 5. $C_{18}H_{37}NO$ requires *M*,283.286 4); τ (−20 °C) 5.39 (s, $CO\overset{-}{C}H\overset{+}{N}$), 6.32—6.49 (m, $\overset{+}{N}CH_2$), 6.78 (s, $\overset{+}{N}Me_2$), 8.23—8.52 (m, $\overset{+}{N}CH_2CH_2$), 8.73 (br s, $[CH_2]_7$), 8.93 (s, CMe_3), and 9.13 (br t, CH_2Me).

Anhydro[benzyldimethyl-(3,3-dimethyl-2-oxobutyl)ammonium hydroxide] (12m) was obtained (81% yield) as colourless prisms, m.p. 60 °C (Found: M^+, 233. $C_{15}H_{23}NO$ requires *M*, 233); τ (−20 °C) 2.61 (s, Ph), 5.07 (s, $\overset{+}{N}CH_2Ph$), 5.56 (br s, $CO\overset{-}{C}H\overset{+}{N}$), 6.84 (s, $\overset{+}{N}Me_2$), and 8.90 (s, CMe_3).

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* Typically the $M^+ - 2$ peak was much stronger than that for M^+.

Anhydro[*trimethyl*-(3,3-*dimethyl*-2-*oxobutyl*)*ammonium hydroxide*] (12n) was obtained (*ca*. 100% yield) as colourless prisms, m.p. 171—172 °C (Found: M^+, 157.146 4. $C_9H_{19}NO$ requires M, 157.146 7); τ 6.65 (s, $\overset{+}{N}Me_3$) and 8.98 (s, CMe_3).

Anhydro-(N-*methyl*-N-*phenacylpyrrolidinium hydroxide*) (14a) was extracted from an aqueous solution into methylene chloride. The extract was evaporated and the residue shaken with dry ether to leave the ylide (14a) (72% yield) as a hygroscopic solid (Found: M^+, 203.130 3. $C_{13}H_{17}NO$ requires M, 203.130 3); τ (−20 °C) 2.30—2.90 (m, Ph), 4.76 (s, $CO\overset{-}{C}H\overset{+}{N}$), $A_2B_2X_4$ system, τ_A 5.88, τ_B 6.85, τ_X 8.00 (br m, 8 H of pyrrolidine ring), and 6.68 (s, $\overset{+}{N}Me$).

Anhydro-(2-*methyl*-2-*phenacylisoindolinium hydroxide*) (14b) (with A. J. Pretty) was extracted from an aqueous solution into chloroform. The chloroform solution was dried ($MgSO_4$), filtered, and evaporated to give the *ylide* (14b) which crystallised from ethanol–ether as pale yellow prisms, m.p. 156—157 °C (75% yield) (Found: C, 81.55; H, 6.9; N, 5.7. $C_{17}H_{17}NO$ requires C, 81.25; H, 6.8; N, 5.6%); τ 2.13—2.80 (m, 9 aryl-H), AB system, τ_A 4.17, τ_B 5.47 (J_{AB} 16 Hz, $CH_2\overset{+}{N}CH_2$), and 6.61 (s, $\overset{+}{N}Me$).

Anhydro-(2-*methyl*-2-*phenacyl*-2,3-*dihydro*-1H-*benz*[de]-*isoquinolinium hydroxide*) (14c) (with S. E. Potter) was extracted from an aqueous solution into chloroform. The chloroform solution was dried, filtered, and evaporated to give the *ylide* (14c) which crystallised from ether–ethanol as pale yellow prisms, m.p. 165 °C (82% yield) (Found: C, 83.6; H, 6.4; N, 4.8. $C_{21}H_{19}NO$ requires C, 83.7; H, 6.3; N, 4.7%); τ 2.11—2.89 (m, 11 aryl-H), AB system, τ_A 4.33, τ_B 5.29 (J_{AB} 18 Hz, $CH_2\overset{+}{N}CH_2$), and 6.62 (s, $\overset{+}{N}Me$).

Reaction between Dimethyl-[(p-*nitrobenzyl*)*phenacyl*]*ammonium Bromide* (13p) *and Aqueous Sodium Hydroxide*.—The ylide (12p) could not be isolated in this case since even at 0 °C it evidently undergoes rearrangement to give *NN*-dimethyl-[α-(*p*-nitrobenzyl)phenacyl]amine (19f) (21%) and in addition a considerable quantity of 4,4′-dinitrobibenzyl (73%) of (*cf*. refs. 27 and 28).

Reaction Between Dimethyl-(o-*methylbenzyl*)*phenacylammonium Bromide* (13q) *and Aqueous Sodium Hydroxide*.—The ylide (12q) could not be isolated and only the rearrangement product *NN*-dimethyl-α-(*o*-methylbenzyl)-phenacylamine (19 g) was obtained (*cf*. ref. 29).

Rearrangement of Ylides (3), (12), *and* (14).—The following experiment is typical.

Rearrangement of anhydro[*benzyldimethyl*(*phenacyl*)*ammonium hydroxide*] (3). The ylide (3) (5 g) was placed in a closed tube, previously flushed with N_2, and heated at 53 °C (acetone vapour) for 4 h. The product was dissolved in ether (200 ml) and extracted with hydrochloric acid (3 × 100 ml, 5N). The combined hydrochloric acid extracts were made basic (5N NaOH) and extracted with ether. The ethereal extracts were dried and evaporated to give α-benzyl-*NN*-dimethylphenacylamine (2) which crystallised from light petroleum as pale yellow needles (4.5 g, 90%), m.p. 75—76 °C (lit.,[1] 77—79 °C); $\nu_{max.}$ 1 690 cm^{-1}; τ 2.14 (dd, J 2, 8 Hz, 2 *ortho*-H of PhCO), 2.51—2.70 (m, 3 aryl-H), 2.85 (s, Ph), ABX system, τ_A 7.10, τ_B 6.74, τ_X 5.70 (J_{AB} 13, J_{AX} 4, J_{BX} 9 Hz, $CH_XCH_AH_BPh$), and 7.64 (s, NMe_2).

Under similar conditions the following ylides also gave the product of a Stevens rearrangement.

Anhydro[*benzyldimethyl*-(p-*bromophenacyl*)*ammonium hydroxide*] (12b) gave α-benzyl-*NN*-dimethyl-*p*-bromophenacylamine (19b) (87%), which crystallised from light petroleum as pale yellow needles, m.p. 103 °C (lit.,[2] 106—107 °C); $\nu_{max.}$ 1 680 cm^{-1}; τ, AA′BB′ system, τ_A 2.21, τ_B 2.55 (J_{AB}, $J_{A'B'}$ 8.5 Hz, *p*-BrC_6H_4), 2.86 (s, Ph), ABX system, τ_A 7.09, τ_B 6.77, τ_X 5.76 (J_{AB} 13, J_{AX} 4, J_{BX} 9 Hz, $CH_XCH_AH_B$-Ph), and 7.63 (s, NMe_2).

Anhydro[*benzyldimethyl*-(p-*phenylphenacyl*)*ammonium hydroxide*] (12a) gave α-benzyl-*NN*-dimethyl-*p*-phenylphenacylamine (19a) (90%) which crystallised from light petroleum as yellow prisms, m.p. 102—103 °C (lit.,[24] 103—104 °C); $\nu_{max.}$ 1 680 cm^{-1}; τ, AA′BB′ system, τ_A 2.06 τ_B 2.48 (J_{AB}, $J_{A'B'}$ 8.5 Hz, *p*-PhC_6H_4), 2.46—2.92 (m, 10, aryl-H), ABX system, τ_A 7.09, τ_B 6.71, τ_X 5.67 (J_{AB} 13, J_{AX} 4 Hz, $CH_XCH_AH_BPh$), and 7.62 (s, NMe_2).

Anhydro[*benzyldimethyl*-(p-*nitrophenacyl*)*ammonium hydroxide*] (12c) gave α-benzyl-*NN*-dimethyl-*p*-nitrophenacylamine (19c) (75%) as a gum; $\nu_{max.}$ 1 680 cm^{-1}; τ, AA′BB′ system, τ_A 1.82, τ_B 2.00 (J_{AB}, $J_{A'B'}$ 8.5 Hz, *p*-$O_2NC_6H_4$), 2.84 (s, Ph), ABX system, τ_A 7.06, τ_B 6.71, τ_X 5.76 (J_{AB} 13, J_{AX} 4, J_{BX} 10 Hz, $CH_XCH_AH_BPh$), and 7.61 (s, NMe_2). This product was characterised as the picrate, m.p. 142—144 °C (Found: C, 52.1; H, 4.3; N, 13.5. $C_{23}H_{21}N_5O_{10}$ requires C, 52.4; H, 4.0; N, 13.2%).

Anhydro[*dimethyl*-(p-*methylbenzyl*)*phenacylammonium hydroxide*] (12d) gave *NN*-dimethyl-α-(*p*-methylbenzyl)-phenacylamine (19d) (82%) which crystallised from light petroleum as colourless *needles*, m.p. 67—68 °C (Found: C, 81.0; H, 7.6; N, 5.2%; M^+, 267. $C_{18}H_{21}NO$ requires C, 80.9; H, 7.9; N, 5.2%; M, 267); $\nu_{max.}$ 1 675 cm^{-1}; τ 2.13 (dd, J 2, 8 Hz, 2 *ortho*-H of PhCO), 2.54—2.80 (m, 3 aryl-H), AA′BB′ system, τ_A 2.92, τ_B 3.02 (J_{AB}, $J_{A'B'}$ 9 Hz, *p*-MeC_6H_4), ABX system, τ_A 71.3, τ_B 6.77, τ_X 5.71 (J_{AB} 13, J_{AX} 4, J_{BX} 8 Hz, $CH_XCH_AH_BAr$), 7.63 (s, NMe_2), and 7.77 (s, Ar–*Me*).

Anhydro[*benzyldimethyl*-(3,3-*dimethyl*-2-*oxobutyl*)*ammonium hydroxide*] (12m) gave 4,4-dimethyl-2-dimethylamino-1-phenylpentan-3-one (19e) (77%) which crystallised from light petroleum as colourless *needles*, m.p. 65 °C (Found: C, 77.5; H, 9.7; N, 5.9%; M^+, 233. $C_{15}H_{23}NO$ requires C, 77.2; H, 9.9; N, 6.0%; M, 233); $\nu_{max.}$ 1 695 cm^{-1}; τ 2.73—2.98 (m, 5 aryl-H), ABX system, τ_A 7.31, τ_B 6.98, τ_X 6.24 (J_{AB} 13, J_{AX} 4, J_{BX} 10 Hz, $CH_XCH_AH_BPh$), 7.67 (s, NMe_2), and 9.09 (s, CMe_3).

Anhydro-(2-*methyl*-2-*phenacylisoindolinium hydroxide*) (14b) (5.0 g) (with A. J. Pretty) was heated at 160 °C in a sealed tube (N_2 atmosphere) until the entire sample had melted. The product was extracted into ether and the ether solution washed with hydrochloric acid (3 × 10 ml, 2N). The acidic extract was made basic with sodium hydroxide (45 ml, 2N) and extracted with ether; the ethereal extract was dried and evaporated to give N-*methyl*-3-*benzoyl*-1,2,3,4-*tetrahydroisoquinoline* (20) (3.6 g, 72%) as a yellow liquid; $\nu_{max.}$ 1 680 cm^{-1}; τ 1.90–2.78 (m, 9 aryl-H), ABX system, τ_A 6.80, τ_B 7.18. τ_X 5.88 (J_{AB} 17, J_{AX} 9.5, J_{BX} 6 Hz; CH_AH_B-CH_XN), AB system, τ_A 6.00, τ_B 6.30 (J 16 Hz, CH_AH_BN), and 7.72 (s, NMe). The *methiodide* had m.p. 228 °C after crystallisation from methanol (Found: C, 55.0; H, 4.9; N, 3.3. $C_{18}H_{21}INO$ requires C, 55.0; H, 5.1; N, 3.6%).

Thermolysis of Anhydro[*decyldimethyl*(*phenacyl*)*ammonium hydroxide*] (12e): *Formation of* NN-*Dimethyldecylamine*, trans-1,2-*dibenzoylethylene* (25), trans-1,2,3-*Tribenzoylcyclopropane* (22), *and* 6,7-*Dibenzoyl*-1,3,5-*triphenylcyclopenta*-[c]*pyran* (26).—The ylide (12e) (5.9 g) was heated under

N_2 in a closed tube at 150 °C for 3 h and the product mixture was separated into basic (2.85 g) and non-basic (2.10 g) material using 5N hydrochloric acid. The basic product was identified as *NN*-dimethyldecylamine by its n.m.r. spectrum. The non-basic products were separated by preparative t.l.c. (silica gel, chloroform) to give (*i*) *trans*-1,2-dibenzoylethylene (25) (200 mg); (*ii*) *trans*-1,2,3-tribenzoylcyclopropane (22), m.p. 219 °C (lit.,[30] m.p. 212—213 °C), $\tau(CF_3CO_2H)$ 1.74—1.99 (m, 3 × 2 *ortho*-H of PhCO), 2.25—2.61 (m, 9 aryl-H), AB_2 system, τ_A 5.47, τ_B 5.81 (J_{AB} 5.5 Hz, 3 cyclopropyl-H); and (*iii*) 6,7-dibenzoyl-1,3,5-triphenylcyclopenta[*c*]pyran (26) (400 mg) as dark red needles, m.p. 210 °C (lit.,[16] m.p. 213 °C), $\nu_{max.}$ 1 665, 1 615, 1 600, and 1 580 cm^{-1}.

Thermolysis of Anhydro-(*2-methyl-2-phenacyl-2,3-dihydro-*1H-*benz*[de]*isoquinolinium hydroxide*) (14c). *Formation of* trans-*1,2,3-Tribenzoylcyclopropane* (22) *and 2-Methyl-2,3-dihydro-*1H-*benz*[de]*isoquinoline* (21).—The ylide (14c) (2 g) was heated under nitrogen at 165—168 °C for 5 min. The resulting dark brown gum was extracted with ether and the residual solid crystallised from methanol to give *trans*-1,2,3-tribenzoylcyclopropane (22) (550 mg, 71%) as colourless needles, m.p. 217 °C. The ethereal extract was extracted with dilute HCl and the extract boiled with charcoal, filtered, made basic (10% aqueous NaOH), and the precipitate collected. Recrystallisation from light petroleum gave 2-methyl-2,3-dihydro-1*H*-benz[*de*]isoquinoline (21) (830 mg, 68%), m.p. 60—61 °C, identical with an authentic sample.

Thermolysis of Anhydro-[*t-butyldimethyl*(*phenacyl*)*ammonium hydroxide*] (12g). *Formation of* NN-*Dimethyl-*N-*phenacylamine.*—A solution of the ylide (12g) (200 mg) was heated at 53 °C for 2 h. Evaporation gave a residual colourless oil (130 mg) identified as *NN*-dimethyl-*N*-phenacylamine.

Reaction between Ylides and Aqueous Hydrobromic Acid. Formation of Quaternary Salts.—The ylides reacted with aqueous hydrobromic acid (1 mol equiv., 45%) in methanol or tetrahydrofuran at 0 °C to give the corresponding quaternary ammonium bromides, identified by comparison with authentic samples. The following procedure is typical. Anhydro[benzyldimethyl(phenacyl)ammonium hydroxide] (3) (550 mg) was added to a solution of aqueous hydrobromic acid (200 mg, 45%) in tetrahydrofuran (20 ml) at 0 °C and the temperature maintained at 0 °C for 1 h. The solution was evaporated and the residual solid crystallised from methanol–ether to give benzyldimethyl(phenacyl)-ammonium bromide (1) (550 mg) as colourless prisms, identical (i.r. and n.m.r. spectra) with an authentic sample.

Reaction between Ylides and Dimethyl Acetylenedicarboxylate. Dimethyl 5-Phenylfuran-2,3-dicarboxylate (32a).—A cold (0 °C) solution of dimethyl acetylenedicarboxylate (355 mg) in tetrahydrofuran (5 ml) was added slowly to a stirred suspension of anhydro[benzyldimethyl(phenacyl)-ammonium hydroxide] (3) (678 mg) in tetrahydrofuran (25 ml) cooled in an ice-salt bath. The resulting suspension was stirred at 0 °C for 2 h, allowed to stand at room temperature for 12 h, and diluted with ether (200 ml). The ethereal solution was washed with hydrochloric acid (5N) and water, dried, and evaporated, and the residual oil purified by preparative t.l.c. (silica gel, chloroform) to give *dimethyl 5-phenylfuran-2,3-dicarboxylate* (32a) (450 mg) as colourless prisms, m.p. 68 °C, after recrystallisation from light petroleum (Found: C, 64.9; H, 4.65%; M^+, 260. $C_{14}H_{12}O_5$ requires C, 64.6; H, 4.6%; *M*, 260); $\lambda_{max.}$ 272 nm (ε 15 100); $\nu_{max.}$ 1 725 cm^{-1}; τ 2.06 (s, 4-H), 2.25—2.65 (m, Ph), 6.12 (s, OMe), and 6.17 (s, OMe). The same product (32a) was obtained (85% yield), together with 2-methylisoindoline (43% yield) by the reaction of dimethyl acetylenedicarboxylate with anhydro-(2-methyl-2-phenacyl-isoindolinium hydroxide) (14b). The furan derivative (32a) (81% yield), together with 2-methyl-2,3-dihydro-1*H*-benz[*de*]isoquinoline (21) (79% yield), was also obtained by the reaction of dimethyl acetylenedicarboxylate with anhydro-(2-methyl-2-phenacyl-2,3-dihydro-1*H*-benz[*de*]isoquinolinium hydroxide) (14c).

Dimethyl 5-(*Biphenyl-4-yl*)*furan-2,3-dicarboxylate* (32b) was prepared in a similar manner from dimethyl acetylenedicarboxylate (500 mg) and anhydro[benzyldimethyl-(*p*-phenylphenacyl)ammonium hydroxide] (12a) (1.04 g). The *product* (32b) (600 mg) crystallised from light petroleum as colourless prisms, m.p. 128—129 °C (Found: C, 71.4; H, 4.7%; M^+, 336. $C_{20}H_{16}O_5$ requires C, 71.4; H, 4.8%; *M*, 336); $\lambda_{max.}$ 297 nm (ε 21 700); $\nu_{max.}$ 1 735 cm^{-1}; τ 2.07 (s, 4-H), 2.18—2.68 (m, 9 aryl-H), 6.10 (s, OMe), and 6.18 (s, OMe).

Dimethyl 5-(p-*Bromophenyl*)*furan-2,3-dicarboxylate* (32c) was prepared from dimethyl acetylenedicarboxylate (465 mg) and anhydro[benzyldimethyl-(*p*-bromophenacyl)-ammonium hydroxide] (12b) (1.05 g). The *product* (32c) (700 mg) crystallised from light petroleum as colourless prisms, m.p. 82 °C (Found: C, 49.8; H, 3.0; Br, 23.45%; M^+, 339. $C_{14}H_{11}BrO_5$ requires C, 49.6; H, 3.3; Br, 23.6%; *M*, 339); $\lambda_{max.}$ 283 nm (ε 17 900); $\nu_{max.}$ 1 740 cm^{-1}; τ 2.07 (s, 4-H), 2.46 (s, 4 aryl-H), 6.12 (s, OMe), and 6.17 (s, OMe).

Dimethyl 5-(p-*Nitrophenyl*)*furan-2,3-dicarboxylate* (32d) was prepared from dimethyl acetylenedicarboxylate (230 mg) and anhydro[benzyldimethyl-(*p*-nitrophenacyl)ammonium hydroxide] (12c) (475 mg). The *product* (32d) (235 mg) crystallised from light petroleum as yellow needles, m.p. 139—140 °C (Found: C, 55.4; H, 3.5; N, 4.3%; M^+, 305. $C_{14}H_{11}NO_7$ requires C, 55.1; H, 3.6; N, 4.6%; *M*, 305); $\lambda_{max.}$ 222 infl. (ε 10 800), and 323 nm (ε 15 100); $\nu_{max.}$ 1 730 cm^{-1}; τ, AA′BB′ system, τ_A–1.76, τ_B 2.13 (J_{AB}, $J_{A'B'}$ 9 Hz, *p*-$C_6H_4NO_2$), 2.00 (s, 4-H), 6.07 (s, OMe), and 6.15 (s, OMe).

Dimethyl 5-t-Butylfuran-2,3-dicarboxylate (32e) was prepared from dimethyl acetylenedicarboxylate (720 mg) and anhydro[decyldimethyl-(3,3-dimethyl-2-oxobutyl)ammonium hydroxide] (12l) (1.45 g). The *product* (32e) (1.08 g) was a colourless oil (Found: C, 60.3; H, 6.4%; M^+, 240. $C_{12}H_{15}O_5$ requires C, 60.0; H, 6.7%; *M*, 240); $\lambda_{max.}$ 245 (ε 4 900), and 305 nm (ε 250); $\nu_{max.}$ 1 730 cm^{-1}; τ 2.23 (s, 4-H), 6.14 (s, OMe), 6.22 (s, OMe), and 8.70 (s, CMe_3).

Reaction between Ylides and Phenyl Isocyanate

Reaction between Anhydro[*benzyldimethyl*(*phenacyl*)*ammonium hydroxide*] (3) *and Phenyl Isocyanate. Formation of 5-*(*Benzyldimethylammonium*)*-2,4,6-trioxo-1,3-diphenyl-1,2,3,4-tetrahydropyrimidin-5-olate* (38).—The ylide (3) (1.27 g) was added slowly to a stirred solution of phenyl isocyanate (3.5 ml) in toluene (20 ml) at 0 °C. The resulting mixture was stirred at room temperature for 15 h, filtered, and the filtrate evaporated. The residue was separated by preparative t.l.c. to give benzanilide (200 mg), aniline, *NN′*-diphenylurea (400 mg), and the *ylide* (38) (600 mg) which crystallised from chloroform–light petroleum as colourless prisms, m.p. 210 °C (Found: C, 73.0; H, 5.2; N, 10.0%; M^+, 413. $C_{25}H_{23}N_3O_3$ requires C, 72.7; H, 5.6; N, 10.2%; *M*, 413); $\nu_{max.}$ 1 695, 1 640, and 1 600 cm^{-1}; τ 2.50—2.84

(m, 15 aryl-H), 5.10 (s, $\overset{+}{N}CH_2Ph$), and 6.48 (s, $\overset{+}{N}Me_2$). The ylide (38) (100 mg) reacted with a cold solution of aqueous hydrobromic acid (45%, 100 mg) in methanol (10 ml) to give the corresponding *quaternary salt* (39) (100 mg), m.p. 131—132 °C (Found: C, 60.4; H, 4.7; N, 8.4; Br, 16.6. $C_{25}H_{24}BrN_3O_3$ requires C, 60.7; H, 4.9; N, 8.5; Br, 16.2%); $\nu_{max.}$ 1 705 and 1 695 cm^{-1}; τ(CF_3CO_2H) 2.40—2.72 (m, 15 aryl-H + $COCH\overset{+}{N}$), 4.80 (s, $\overset{+}{N}CH_2Ph$), and 6.20 (s, $\overset{+}{N}Me_2$). The ylide (38) (100 mg) was heated at 200 °C in a closed tube for 2 h, and the product was crystallised from chloroform–light petroleum to give *5-benzyl-5-dimethylamino-2,4,6-trioxo-1,3-diphenylperhydropyrimidine* (40) (90 mg) as colourless prisms, m.p. 227—228 °C [Found: C, 71.2; H, 6.0; N, 9.95%; M^+, 413.173 4. $C_{25}H_{23}N_3O_3\cdot 0.5H_2O$ requires C, 71.1; H, 5.7; N, 9.95%; M ($C_{25}H_{23}N_3O_3$), 413.173 9]; $\nu_{max.}$ 1 695 cm^{-1}; τ 2.60—3.15 (m, 15 aryl-H), 6.48 (s, CH_2Ph), and 7.36 (s, NMe_2).

Reaction of Anhydro-(2-methyl-2-phenacylisoindolinium hydroxide) (14b) with Phenyl Isocyanate. Formation of Anhydro-[2-methyl-2-(N-phenylcarbamoylmethyl)isoindolinium Hydroxide] (35a).—Phenyl isocyanate (1.9 g) was added to a stirred solution of the ylide (14b) (2.0 g) in chloroform (10 ml) at −5 °C. The reaction mixture was left at 0 °C for 3 h and at room temperature overnight, and evaporated. The residue crystallised from ethanol–ether to give the *ylide* (35a) (1.6 g, 76%) as colourless plates, m.p. 179—181 °C (Found: C, 76.2; H, 6.9; N, 10.4. $C_{17}H_{18}N_2O$ requires C, 76.7; H, 6.8; N, 10.5%); $\nu_{max.}$ 1 600 and 1 575 cm^{-1}; τ 2.50—3.18 (m, 9 aryl-H + $\overset{+}{N}CH{=}C{-}O^-$ + NH), AB system, τ_A 4.8, τ_B 5.3 (J_{AB} 15 Hz, 2 × $\overset{+}{N}CH_2Ar$), and 6.62 (s, $\overset{+}{N}Me$). The mother-liquors were evaporated and the residue purified by chromatography (silica gel, benzene–chloroform) to give benzanilide (0.5 g). The ylide (35a) reacted with toluene-*p*-sulphonic acid to give the *quaternary salt* (36a; X = p-$MeC_6H_4SO_3$), m.p. 151 °C (from benzene) (Found: C, 66.0; H, 6.2; N, 6.5; S, 7.1. $C_{24}H_{26}N_2O_4S$ requires C, 65.75; H, 5.9; N, 6.4; S, 7.3%); $\nu_{max.}$ 1 680, 1 600, and 1 560 cm^{-1}; τ −0.62 (br s, CON*H*Ph), 2.20—3.10 (m, 13 aryl-H), AB system, τ_A 4.80, τ_B 5.16 (J_{AB} 14 Hz, 2 × $\overset{+}{N}CH_2Ar$), 5.04 (s, $\overset{+}{N}CH_2CO$), 6.99 (s, $\overset{+}{N}Me$), and 7.78 (s, Ar-*Me*).

Reaction of Anhydro-(2-methyl-2-phenacyl-2,3-dihydro-1H-benz[de]isoquinolinium hydroxide) (14c) with Phenyl Isocyanate. Formation of 2-Methyl-2-(N-phenylcarbamoylmethyl)-2,3-dihydro-1H-benz[de]isoquinolinium Chloride (36b; X = Cl).—Phenyl isocyanate (800 mg) in chloroform (3 ml) was added to a stirred solution of the ylide (14c) (1.0 g) in chloroform (10 ml) at 0 °C. The reaction mixture was stirred at 0—5 °C for 4 h and evaporated; the residual brown gum was dissolved in ethanol (10 ml) and treated with dry hydrogen chloride gas. Anhydrous ether (25 ml) was added and the solution kept at 0 °C overnight; the resulting crystals were collected and recrystallised from ethanol–ether to give the *salt* (36b; X = Cl) (900 mg, 77%), m.p. 216—217 °C (Found: C, 71.1; H, 6.3; N, 8.1; Cl, 10.2. $C_{21}H_{21}ClN_2O$ requires C, 71.5; H, 6.0; N, 7.9; Cl, 10.1%); $\nu_{max.}$ (Nujol) 1 680, 1 600, and 1 555 cm^{-1}; τ(CF_3CO_2H) 0.85 (s, CON*H*Ph), 1.90—2.85 (m, 11 aryl-H), AB system, τ_A 4.58, τ_B 4.87 (J_{AB} 15 Hz, 2 × $\overset{+}{N}CH_2Ar$), 5.51 (s, $\overset{+}{N}CH_2CO$), and 6.31 (s, $\overset{+}{N}Me$).

Reaction between Ylides and Methyl Iodide

Reaction between Anhydro[benzyldimethyl(phenacyl)ammonium hydroxide] (3) and Methyl Iodide. Formation of Benzyldimethyl-(α-methylphenacyl)ammonium Iodide (41a).—The ylide (3) (5.0 g) was added to a stirred solution of methyl iodide (10 ml) in tetrahydrofuran (25 ml) at 0 °C. The resulting solution was kept at 0 °C for 12 h and evaporated, and the residue crystallised from methanol–ether giving colourless prisms (2.5 g). The n.m.r. spectrum of this product showed that it was a mixture of the salt (41a) and benzyldimethyl(phenacyl)ammonium iodide, in the ratio 6 : 1.

Under similar conditions the ylide (14b) gave 2-methyl-2-(α-methylphenacyl)isoindolinium iodide (41b) and 2-methyl-2-phenacylisoindolinium iodide in a ratio of 2 : 1 [n.m.r. spectrum, τ 3.95 (q, *J* 7 Hz, $\overset{+}{N}CHMeCO$) and 8.05 (d, *J* 7 Hz, $\overset{+}{N}CHMe$) assignable to the salt (41b), and τ 4.32 (s, $\overset{+}{N}CH_2CO$) assignable to the salt (15b; I in place of Br)], and the ylide (14c) gave 2-methyl-2-(α-methylphenacyl)-2,3-dihydro-1*H*-benz[*de*]isoquinolinium iodide (41c) and 2-methyl-2-phenacyl-2,3-dihydro-1*H*-benz[*de*]isoquinolinium iodide in the ratio 6 : 1 [n.m.r. spectrum, τ 6.32 (s, $\overset{+}{N}Me$) assignable to the salt (40c), and τ 6.24 (s, $\overset{+}{N}Me$) assignable to the salt (15c; I in place of Br)].

Reaction of Anhydro-(2-methyl-2-phenacyl-2,3-dihydro-1H-benz[de]isoquinolinium hydroxide) (14c) with Benzoyl Chloride. Formation of 2-Methyl-2-(2-benzoyloxy-2-phenylvinyl)-2,3-dihydro-1H-benz[de]isoquinolinium Chloride (42).—Benzoyl chloride (250 mg) in dry tetrahydrofuran (3 ml) was added to a stirred solution of the ylide (14c) (500 mg) in dry tetrahydrofuran (5 ml) and the mixture left overnight at room temperature. Evaporation gave a solid which crystallised from ethanol–ether to give the *salt* (42) (630 mg, 86%), m.p. 145—147 °C (Found: C, 75.9; H, 5.3; N, 3.2; Cl, 8.0. $C_{28}H_{22}ClNO_2$ requires C, 76.1; H, 5.4; N, 3.2; Cl, 8.0%); $\nu_{max.}$ 1 760 and 1 600 cm^{-1}; τ 1.70—3.10 (m, 16 aryl-H), 3.31 (s, $\overset{+}{N}CH{=}C$), AB system, τ_A 3.82, τ_B 4.32 (J_{AB} 15 Hz, 2 × $\overset{+}{N}CH_2Ar$), and 5.84 (s, $\overset{+}{N}Me$).

Reaction between Anhydro[benzyldimethyl(phenacyl)ammonium hydroxide] (3) and trans-*1,2-Dibenzoylethylene. Formation of* trans-*1,2,3-Tribenzoylcyclopropane (22) and 6,7-Dibenzoyl-1,3,5-triphenylcyclopenta[c]pyran* (26).—The ylide (3) (1.36 g) was added to a solution of *trans*-1,2-dibenzoylethylene (1.18 g) in tetrahydrofuran at 0 °C. The solution was left at 0 °C for 12 h and at room temperature for 12 h, diluted with chloroform (200 ml), washed successively with hydrochloric acid (3 × 50 ml, 5N) and water, dried, and evaporated. The residue was separated by chromatography (silica, chloroform) to give *trans*-tribenzoylcyclopropane (22) (400 mg) and the cyclopentapyran (26) (100 mg).

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