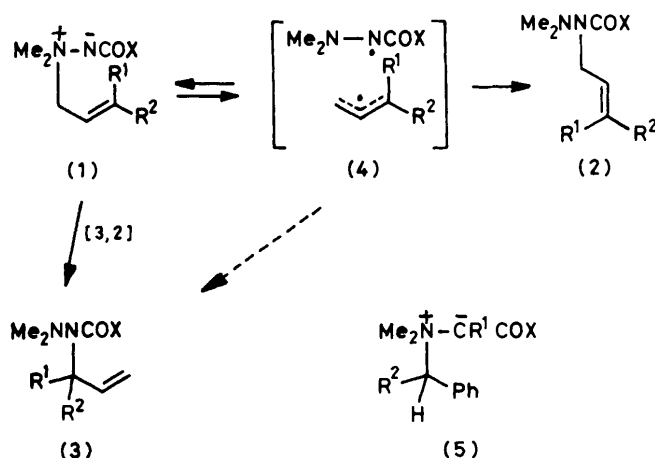


Base Catalysed Rearrangements involving Ylide Intermediates. Part 17.¹ The Preparation and Thermal Rearrangement of Pentadienylammonioamidates

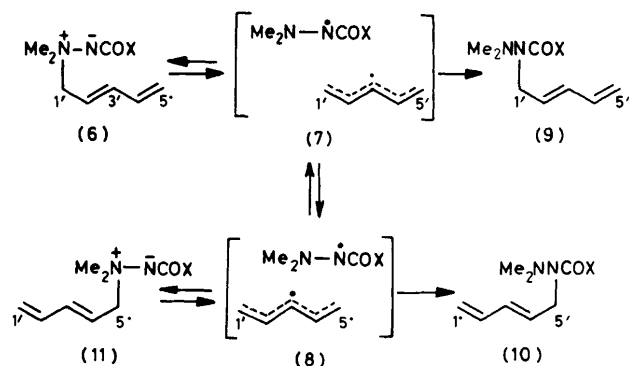
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The thermal rearrangements of the (2'E)-penta-2',4'-dienylammonioamidates (13) give products (14) and (15) that are formally derived from [1,2] and [5,2] rearrangements and, in some cases, the product (16) of a [3,2] rearrangement. The products (14) and (15) are formed by a radical mechanism in which (a) radical recombination to give the products (14) and (15) competes with recombination to give the ammonioamidates (13) and (19) and (b) the translational equilibration of the radical pairs (7) and (8) is fast compared with radical pair recombination and diffusion to give free radicals.

The thermal rearrangements of allylammonioamidates (1; X = Me, OEt, NHMe, NHPh) were discussed in a previous paper in this series.¹ The ylides (1) rearrange by two major pathways: a [1,2] rearrangement (1) → (2) probably involving a radical pair mechanism, and a [3,2] rearrangement (1) → (3) which probably proceeds by a concerted pericyclic mechanism. The study of the rearrangements of the ammonioamidates (1) was made more complicated by the observation that the radical pair (4), involved as an intermediate in the process (1) → (2), undergoes recombination to give the starting ylide (1) in addition to the product (2) (Scheme 1). The proposed intermediacy of the radical pair (4) in the process (1) → (2) was based upon 'mixing' experiments of the same type as those used in our earlier investigation² of the Stevens [1,2] rearrangement of ammonium ylides such as (5). These experiments established that diffusion from the radical pair (4) to give free radicals competed with recombination to give the products (1) or (2). It was of interest therefore to use a probe for a radical pair intermediate that would detect a radical pair having an even shorter lifetime τ than that required for competitive diffusion to give free radicals (τ ca. 10^{-10} – 10^{-11} s). A migrating penta-2',4'-dienyl substituent would provide such a probe † since it could be expected that for a penta-2',4'-dienylammonioamidate (6), yielding the radical pair (7), random recombination involving positions 1' and 5' of the pentadienyl component would require less time than that required for diffusion to give free radicals. Thus the limited translational motion indicated by (7) ⇌ (8) in Scheme 2 would suffice for 1',5'-scrambling and a process involving a very short-lived radical pair (lifetime $\tau < 10^{-11}$ s) might still give complete 1',5'-scrambling to give the products (9) and (10), formally derived from [1,2] and [5,2] rearrangements. These possibilities for the rearrangement of penta-2',4'-dienylammonioamidates involving radical pair intermediates are summarised in Scheme 2. The additional possibilities of a concerted [3,2] rearrangement and radical coupling involving position 3' of the pentadienyl component of the radical pair (7) or (8) are omitted from this scheme but it will be shown subsequently that in some cases 3'-coupling, by either the concerted or radical pair mode, does lead to some reaction products. By analogy with our earlier studies¹ (see Scheme 1) radical pair recombination to give either the starting ylide (6) or the 'scrambled' ylide (11) is included in the Scheme.



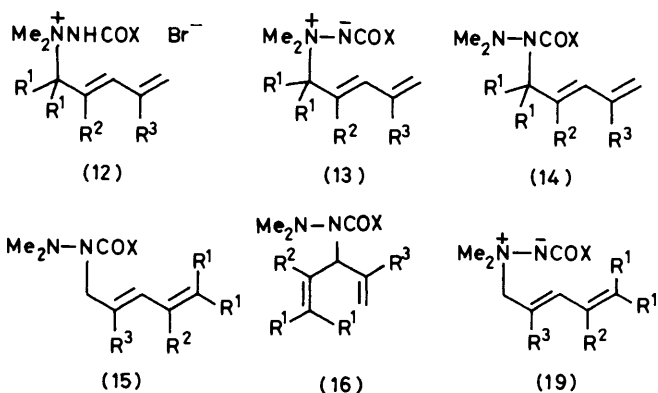
Scheme 1. Rearrangement reactions of allylammonioamidates. The possible involvement of the radical pair (4) in the formation of some of the product (3) is indicated by the broken arrow



Scheme 2. Radical pair reactions of pentadienylammonioamidates (6). The identities of the terminal carbon atoms of the pentadienyl component are indicated by the labels 1' and 5'

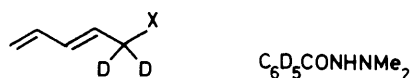
† Other probes that have been used to detect short-lived radical intermediates include CIDNP⁴ ($\tau > 10^{-8}$ s), loss of stereochemical configuration^{2,3} (τ ca. 10^{-10} – 10^{-11} s), and intramolecular cyclisation of a hexenyl radical.⁵

The penta-2',4'-dienylhydrazinium salts (12) were synthesised by the reaction of the appropriate hydrazine derivative with the pentadienyl bromide. The salts (12) reacted with base to give the ammonioamidates (13) as gums or crystalline solids, characterised by their spectroscopic properties and molecular formulae (elemental analysis or high-



in (12)–(16):
and (19)

- a; $R^1 = R^2 = R^3 = H$, $X = Me$
 b; $R^1 = D$, $R^2 = R^3 = H$, $X = Me$
 c; $R^1 = R^3 = H$, $R^2 = X = Me$
 d; $R^1 = R^2 = H$, $R^3 = X = Me$
 e; $R^1 = R^2 = R^3 = H$, $X = OEt$
 f; $R^1 = D$, $R^2 = R^3 = H$, $X = OEt$
 g; $R^1 = R^3 = H$, $R^2 = Me$, $X = OEt$
 h; $R^1 = R^2 = H$, $R^3 = Me$, $X = OEt$
 i; $R^1 = R^2 = R^3 = H$, $X = NHMe$
 j; $R^1 = D$, $R^2 = R^3 = H$, $X = NHMe$
 k; $R^1 = R^3 = H$, $R^2 = Me$, $X = NHMe$
 l; $R^1 = R^2 = H$, $R^3 = Me$, $X = NHMe$
 m; $R^1 = R^3 = H$, $R^2 = Me$, $X = NPh$
 n; $R^1 = R^2 = H$, $R^3 = Me$, $X = NPh$
 o; $R^1 = R^2 = R^3 = H$, $X = Ph$
 p; $R^1 = D$, $R^2 = R^3 = H$, $X = C_6D_5$



(17) $X = Br$

(18) $X = OH$

(20)

resolution mass spectrum). The ammonioamidates (13) rearranged on heating in dry benzene to give the products (14) and (15), corresponding formally to the products of [1,2] and [5,2] rearrangements, and in some cases the product (16) of a [3,2] rearrangement. The deuterated salts (12b), (12f), (12j), and (12p) were prepared using $[1,1\text{-}^2H_2]$ pentadienyl bromide (17) obtained from the reaction of the $[1,1\text{-}^2H_2]$ -dienol (18) with phosphorus tribromide.

The compositions of the reaction products from the rearrangement of the ammonioamidates (13) are summarised in Table 1. Two general conclusions can be drawn from these results.⁶ (a) The ratio of [1,2] and [5,2] products depends upon the structure of the pentadienyl group in a manner that is consistent with the derivation of these products from a radical pair analogous to (7) in which the translational motion required for the equilibration analogous to (7) \rightleftharpoons (8) is fast compared with radical coupling. (b) The extent of the competing [3,2] rearrangement depends upon the structure of the starting ylide and is not consistent with the derivation of this product from a radical pair analogous to (7). We conclude that the product (16) is, at least in part, derived from a concerted pericyclic process⁷ that competes with the homolytic pathway for rearrangement. These conclusions are similar to those drawn from our earlier examination¹ of the rearrangements of allylammonioamidates and it was, therefore, of interest to determine the extent to which radical pair recombination to give the ammonioamidates analogous to (6) and (11) compared with the formation of the rearrangement products (14), (15), and (16). This possibility was examined using either the $[1',1'\text{-}^2H_2]$ pentadienylammonioamidates (13f) and (13p) or the 2'-methylpentadienylammonioamidates (13c), (13g), (13k), and (13m). The products of partial rearrangement were studied by n.m.r. spectroscopy to determine the extent to which the ammonioamidate had undergone 1',5'-pentadienyl 'scrambling' [(13) \rightleftharpoons (19)] and rearrangement [(13) \rightarrow (14) + (15) + (16)] at measured times. The product compositions could be used to obtain approximate rate constants for the processes summarised in Scheme 3 (Experimental section). The results of this examination (Table 3; Experimental section), although of limited quantitative significance due to the difficulty of obtaining sufficiently accurate product compositions by n.m.r. measure-

Table 1. Thermal rearrangement of penta-2',4'-dienylammonioamidates (13) in benzene at 80 °C

	Ammonioamidate (13)				Time (h)	Product ratio ^a		
	X	R ¹	R ²	R ³		[1,2]	[5,2]	[3,2]
(13p)	C ₆ D ₅	D	H	H	48	1	1	<i>b</i>
(13c)	Me	H	Me	H	36	1	2	<i>b</i>
(13d)	Me	H	H	Me	36	2	1	<i>b</i>
(13b)	Me	D	H	H	36	1	1	<i>b</i>
(13g)	EtO	H	Me	H	6	1	2	0.5
(13h)	EtO	H	H	Me	6	2	1	0.8
(13f)	EtO	D	H	H	8	1	1	0.3
(13k)	MeNH	H	Me	H	3	1	2	0.8
(13l)	MeNH	H	H	Me	3	2	1	1.5
(13j)	MeNH	D	H	H	6	1	1	0.6
(13m)	PhNH	H	Me	H	6	1	2	0.7
(13n)	PhNH	H	H	Me	6	2	1	1.0

^a Based upon isolated products (14), (15), and (16) or n.m.r. integration in cases where products could not be separated. ^b This product was not formed in sufficient quantity for isolation.

Table 2. Intramolecularity in the [1,2] and [5,2] rearrangement of the [$^2\text{H}_0$]- and [$^2\text{H}_1$]-penta-2',4'-dienylammonioamidates (13o) + (13p)

Reaction conditions				Product ratio ^a [1,2]/[5,2]	Intra- molecularity ^b (%)
Solvent	Temp. (°C)	Viscosity (cP)	Time (h)		
Glycerol	100	14.8	120	1.2	92
Glycerol	160	3.28	8	1.0	55
Ethylene glycol	80	3.02	168	1.0	69
Ethylene glycol	100	1.99	72	1.0	60
Butanol	100	0.54	48	1.0	30
Benzene	80	0.33	48	1.0	17
Methyl cyanide	80	0.22	60	1.0	9

^a Based upon the position of the deuterium label in the pentadienyl side chain of the rearrangement product (14p) + (15p) of the [$^2\text{H}_1$]ammonioamidate (13p) as indicated by integration of the NCH_2 - and $\text{C}=\text{CH}_2$ signals in the n.m.r. spectrum of the reaction product.

^b For the rearrangement of a 1 : 1 mixture of the [$^2\text{H}_0$]- (13o) and [$^2\text{H}_1$]- (13p) ammonioamidates with (100 - 4z)% intramolecularity the reaction product contains z% of the [$^2\text{H}_2$] and z% of the [$^2\text{H}_3$] products.

ments, show that in all cases the rate of 1',5'-pentadienyl scrambling in the ammonioamidate is comparable with the overall rate of rearrangement, but in only one case (13m) is it actually faster than the rate of rearrangement. Thus although the product ratios recorded in Table 1 may be modified by 1',5'-pentadienyl scrambling (13) \rightleftharpoons (19) the two general conclusions, (a) and (b), drawn from these results do not require modification.

It was also of interest to determine the extent to which the rearrangement reactions of the pentadienylammonioamidates were intramolecular in solvents of varying viscosity² and whether, in very viscous solvents, the translational motion required for the radical pair equilibration (7) \rightleftharpoons (8) would become slow compared with the radical pair recombination to give the products (9) and (10). The ammonioamidate (13o) was chosen for this study since the heptadeuterio-derivative (13p) could be synthesised readily using [1,1- $^2\text{H}_2$]penta-2,4-dienyl bromide (17) and 1-[$^2\text{H}_3$]benzoyl-2,2-dimethylhydrazine (20). The determination of the intramolecularity of the rearrangement was carried out as in our earlier investigation² of the mechanism of the Stevens [1,2] rearrangement of ammonium ylides and the results are summarised in Table 2. As expected, the intramolecularity of the rearrangement is only high in solvents of high viscosity, but even under conditions where the rearrangement shows considerable intramolecularity (>50%) the ratio of the products of [1,2] and [5,2] coupling indicates that the translational equilibration (7) \rightleftharpoons (8) is complete in all but one case[†] before radical pair recombination takes place. This probe⁸ for the detection of short-lived radical intermediates is therefore likely to prove more sensitive than the more conventional probes based upon the retention of configuration of the migrating group and intramolecularity. This conclusion will be exploited in future papers in this series.

Experimental

For general directions see Part 1.⁹

(2E)-[1,1- $^2\text{H}_2$]Penta-2,4-dienol (18).—A solution of ethyl (2E)-penta-2,4-dienoate¹⁰ (7.0 g) in anhydrous ether (50 ml)

was added slowly to a suspension of lithium aluminium deuteride (2.30 g) in anhydrous ether (50 ml) at -20 °C, and the mixture was stirred at room temperature for 3 h. Excess of reducing agent was destroyed by the addition of wet ether, the mixture acidified by dropwise addition of aqueous sulphuric acid (20%), and the ether layer separated by decanting. The aqueous layer was washed with ether and the combined ether extracts were dried and evaporated. The residual oil was distilled to give the deuterated dienol (18) as a colourless liquid (3.80 g, 77%), b.p. 72–75 °C at 11 mmHg; δ 6.54–6.13 (m, CH-CH), 5.81br (d, J 15 Hz, CD_2 -CH=) 5.05–5.30 (m, C=CH₂), and 2.22 (s, OH), with no detectable signal for the OCH₂ group (δ 4.15) indicating >99 atom % D at C-1.

(2E)-[1,1- $^2\text{H}_2$]Penta-2,4-dienyl Bromide (17).—This was prepared from the above dienol by reaction with phosphorus tribromide in dry pyridine at 0 °C. The product (78% yield) was used without distillation.

Preparation of Hydrazinium Salts (12).—An equimolar mixture of 1-acetyl-2,2-dimethylhydrazine, 1-ethoxycarbonyl-2,2-dimethylhydrazine, 1,1-dimethyl-4-phenylsemicarbazide, or 1,1,4-trimethylsemicarbazide, and the appropriate dienyl bromide in methyl cyanide, was stirred at room temperature for 12 h. The reaction mixture was concentrated by evaporation and the salt precipitated by the addition of dry ether and recrystallised from ethanol-ether. Most hydrazinium salts were obtained as solids but the salts from 1,1,4-trimethylsemicarbazide were gums which were converted into the corresponding ylides without further purification. The following salts were prepared by this method.

2-Acetyl-1,1-dimethyl-1-[(2'E)-penta-2',4'-dienyl]hydrazinium bromide (12a). This was obtained as crystals, m.p. 108–109 °C (82%) (Found: C, 43.5; H, 6.8; Br, 32.2; N, 11.5. $\text{C}_9\text{H}_{17}\text{BrN}_2\text{O}$ requires C, 43.4; H, 6.8; Br, 32.1; N, 11.3%); ν_{max} (Nujol) 3 120, 1 703, and 1 600 cm^{-1} ; $\delta(\text{CD}_3\text{OD})$ 6.80–6.30 (m, =CH-CH=), 5.84 (dt, J 15 and 7 Hz, CH=CH-CH₂), 5.55–5.27 (m, C=CH₂), 5.33 (d, J 7 Hz, NCH₂), 3.62 (s, NMe₂), and 2.05 (s, COCH₃).

2-Acetyl-1,1-dimethyl-1-[(2'E)-[1',1'- $^2\text{H}_2$]penta-2',4'-dienyl]hydrazinium bromide (12b). This was obtained as crystals, m.p. 108–109 °C (80%) (Found: C, 43.25; H, * 7.0; Br, 32.1; N, 11.3. $\text{C}_9\text{H}_{15}\text{D}_2\text{BrN}_2\text{O}$ requires C, 43.0; H, * 6.8; Br, 31.9; N, 11.15%); $\delta(\text{CD}_3\text{OD})$ 6.77–6.35 (m,

[†] The n.m.r. spectrum of the product from the rearrangement in glycerol at 100 °C shows a slight preponderance of [1,2] coupling, but in view of the errors inherent in the integration of n.m.r. signals ($\pm 10\%$ estimated error) the estimated ratio of 1.2 (Table 2) can hardly be regarded as being significantly different from the ratio of 1.0 found for all other cases.

* For this and other deuterated compounds the value refers to the combined D and H content estimated as H.

=CH=CH=), 5.85 (d, J 15 Hz, CH=CH-CD₂), 5.54—5.30 (m, C=CH₂), 3.63 (s, NMe₂), and 2.06 (s, COCH₃), with no detectable signal for the NCH₂ group corresponding to >95 atom % D at C-1'.

2-Acetyl-1,1-dimethyl-1-(2'-methylpenta-2',4'-dienyl)hydrazinium bromide (12c). This was obtained as crystals (88%) (Found: C, 42.1; H, 6.9; Br, 28.6; N, 10.2. C₁₀H₁₉BrNO requires C, 42.7; H, 7.5; Br, 28.5; N, 10.0%); ν_{\max} 1 700 cm⁻¹; δ (CD₃OD) ABXY system, δ_A 6.69, δ_B 6.40, δ_X 5.46, δ_Y 5.39 (J_{AB} 10, J_{AX} 16, J_{AY} 10 Hz, CH_B-CH_A=CH_XH_Y), 4.74 (s, NCH₂), 3.67 (s, NMe₂), 2.07 (s, COCH₃), and 1.99 (s, C=CMe).

2-Acetyl-1,1-dimethyl-1-(4'-methylpenta-2',4'-dienyl)hydrazinium bromide (12d). This was obtained as crystals (82%); ν_{\max} 1 700 cm⁻¹; δ (CD₃OD) AMX₂ system, δ_A 6.70, δ_M 5.71, δ_X 4.91 [J_{AM} 15, J_{MX} 7 Hz, CH_A=CH_M-C(H_X)₂], 5.20br (s, C=CH₂), 3.85 (s, NMe₂), 2.21 (s, COCH₃), and 1.93 (s, C=CMe).

2-Ethoxycarbonyl-1,1-dimethyl-1-[(2'E)-penta-2',4'-dienyl]hydrazinium bromide (12e). This was obtained as crystals, m.p. 89—90 °C (82%) (Found: C, 43.1; H, 7.05; Br, 28.7; N, 10.3. C₁₀H₁₉BrN₂O₂ requires C, 43.0; H, 6.8; Br, 28.7; N, 10.1%); ν_{\max} (Nujol) 3 480—3 380, 1 742, 1 650, and 1 608 cm⁻¹; δ (CD₃OD) 6.76—6.30 (m, =CH=CH=), 5.82 (dt, J 15, 7.5 Hz, CH=CH-CH₂), 5.56—5.28 (m, C=CH₂), 4.62 (d, J 7.5 Hz, NCH₂), A₂X₃ system, δ_A 4.24, δ_X 1.27 [J_{AX} 7 Hz, OC(H_A)₂C(H_X)₃], and 2.60 (s, NMe₂).

2-Ethoxycarbonyl-1,1-dimethyl-1-[(2'E)-[1',1'-²H₂]penta-2',4'-dienyl]hydrazinium bromide (12f). This was obtained as colourless crystals, m.p. 88—90 °C (80%) (Found: C, 42.85; H, 7.0; Br, 28.6; N, 9.6. C₁₀H₁₇D₂BrN₂O₂ requires C, 42.7; H, 6.8; Br, 28.5; N, 9.6%); δ (CD₃OD) 6.77—6.31 (m, =CH=CH=), 5.82 (d, J 15 Hz, CH=CH-CD₂), 5.60—5.25 (m, C=CH₂), A₂X₃ system, δ_A 4.25, δ_X 1.28 [J_{AX} 7 Hz, OC(H_A)₂C(H_X)₃], and 2.60 (s, NMe₂), with no detectable signal for CH₂N⁺ corresponding to >95 atom % D at C-1'.

2-Ethoxycarbonyl-1,1-dimethyl-1-[(2'E)-2'-methylpenta-2',4'-dienyl]hydrazinium bromide (12g). This was obtained as crystals, m.p. 101—103 °C (75%) (Found: C, 45.0; H, 7.3; Br, 27.1; N, 9.3. C₁₁H₂₁BrN₂O₂ requires C, 45.1; H, 7.2; Br, 27.2; N, 9.55%); ν_{\max} 1 745 cm⁻¹; δ 6.66—6.36 (m, =CH-CH), 5.60—5.25 (m, C=CH₂), 4.94 (s, NCH₂), A₂X₃ system, δ_A 4.24, δ_X 1.28 [J_{AX} 7 Hz, OC(H_A)₂C(H_X)₃], 3.87 (s, NMe₂), and 2.00 (s, C=CMe).

2-Ethoxycarbonyl-1,1-dimethyl-1-[(2'E)-4'-methylpenta-2',4'-dienyl]hydrazinium bromide (12h). This was obtained as a gum, contaminated with the hydrobromide salt, which was converted into the ylide without further purification; δ (CD₃-OD) AMX₂ system, δ_A 6.72, δ_M 5.76, δ_X 4.72 [J_{AM} 15, J_{MX} 7.5 Hz, CH_A=CH_M-C(H_X)₂], 5.21br (s, C=CH₂), A₂X₃ system, δ_A 4.28, δ_X 1.30 [J_{AX} 7 Hz, OC(H_A)₂C(H_X)₃], 3.27 (s, NMe₂), and 1.93 (s, C=CMe).

1,1-Dimethyl-2-methylcarbamoyl-1-[(2'E)-penta-2',4'-dienyl]hydrazinium bromide (12i). This was obtained as a gum which was converted into the corresponding ylide without further purification; δ (CD₃OD) 6.78—6.30 (m, =CH=CH=), 5.86 (dt, J 7, 14 Hz, CH=CH-CH₂), 5.51—5.27 (m, C=CH₂), 4.64 (d, J 7 Hz, NCH₂), 3.60 (s, NMe₂), and 2.72 (s, CONHMe).

1,1-Dimethyl-2-methylcarbamoyl-1-[(2'E)-[1',1'-²H₂]penta-2',4'-dienyl]hydrazinium bromide (12j). This was obtained as a gum which was converted into the corresponding ylide without further purification; δ (CD₃OD) 6.78—6.30 (m, =CH=CH=),

5.83 (d, J 14 Hz, CH=CH-CD₂), 5.52—5.28 (m, C=CH₂), 3.58 (s, NMe₂), and 2.73 (s, CONHMe), with no detectable signal for CH₂N⁺ corresponding to >95% atom % D at C-1'.

1,1-Dimethyl-2-methylcarbamoyl-1-[(2'E)-2'-methylpenta-2',4'-dienyl]hydrazinium bromide (12k). This was obtained as a gum (70%) which was converted into the corresponding ylide without further purification; δ (CD₃OD), ABXY system, δ_A 6.70, δ_B 6.50, δ_X 5.40, δ_Y 5.36 (J_{AB} 10, J_{AX} 16, J_{AY} 10 Hz, =CH_A-CH_B=CH_XH_Y), 4.64 (s, NCH₂), 3.59 (s, NMe₂), 2.74 (s, CONHMe), and 1.99 (s, C=CMe).

1,1-Dimethyl-2-methylcarbamoyl-1-[(2'E)-4'-methylpenta-2',4'-dienyl]hydrazinium bromide (12l). This was obtained as a gum (72%) which was converted into the corresponding ylide without further purification; δ (CD₃OD), AMX₂ system, δ_A 6.70, δ_M 5.79, δ_X 4.67 [J_{AM} 15, J_{MX} 7 Hz, CH_A=CH_M-C(H_X)₂], 5.19 (s, C=CH₂), 3.60 (s, NMe₂), 2.72 (s, CONHMe), and 1.92 (s, C=CMe).

1,1-Dimethyl-1-[(2'E)-2'-methylpenta-2',4'-dienyl]-2-phenylcarbamoylhydrazinium bromide (12m). This was obtained as crystals, m.p. 116—118 °C (85%) (Found: C, 52.8; H, 6.8; Br, 23.3; N, 12.2. C₁₅H₂₂BrN₃O requires C, 52.9; H, 6.5; Br, 23.5; N, 12.35%); ν_{\max} 3 260, 3 200, 3 140, 1 720, and 1 605 cm⁻¹; δ (CD₃OD) 7.50—7.06 (m, 5 aryl H), ABXY system, δ_A 6.62, δ_B 6.40, δ_X 5.41, δ_Y 5.37 (J_{AB} 10, J_{AX} 16, J_{AY} 10 Hz, =CH_B-CH_A=CH_XH_Y), 4.69 (s, NCH₂), 3.67 (s, NMe₂), and 2.05 (s, C=CMe).

1,1-Dimethyl-1-[(2'E)-4'-methylpenta-2',4'-dienyl]-2-phenylcarbamoylhydrazinium bromide (12n). This was obtained as a hygroscopic solid (87%); δ [(CD₃)₂CO] 7.02—7.56 (m, 5 aryl H), ABX₂ system, δ_A 6.77, δ_B 6.01, δ_X 4.84 [J_{AB} 15, J_{BX} 8 Hz, CH_A=CH_B-C(H_X)₂], 5.15 (s, C=CH), 5.10 (s, C=CH), 3.79 (s, NMe₂), and 1.96 (s, C=CMe).

2-Benzoyl-1,1-dimethyl-1-[(2'E)-penta-2',4'-dienyl]hydrazinium bromide (12o). This was obtained as crystals, m.p. 112—114 °C (87%) (Found: C, 54.2; H, 6.1; Br, 25.7; N, 9.2. C₁₄H₁₉BrN₂O requires C, 54.0; H, 6.1; Br, 25.7; N, 9.0%); ν_{\max} (Nujol) 1 690 and 1 605 cm⁻¹; δ 7.99 (dd, J 8, 1.5 Hz, 2 ortho-H of C₆H₅), 7.63—7.33 (m, 3 aryl H), ABMXYZ₂ system, δ_A 6.64, δ_B 6.33, δ_M 5.76, δ_X 5.36, δ_Y 5.29, δ_Z 5.05 [J_{AB} 10, J_{AM} 14, J_{BX} 16, J_{BY} 10, J_{MZ} 7 Hz, N⁺C(H_Z)₂-CH_M=CH_A-CH_B=CH_XH_Y], and 3.87 (s, NMe₂).

2-[²H₅]Benzoyl-1,1-dimethyl-1-[(2'E)-[1',1'-²H₂]penta-2',4'-dienyl]hydrazinium bromide (12p). This was obtained as crystals, m.p. 112—114 °C (85%) (Found: C, 52.7; H, 6.1; Br, 25.3; N, 8.8. C₁₄H₁₂D₇BrN₂O requires C, 52.8; H, 6.0; Br, 25.2; N, 8.8%); δ ABMX₂ system, δ_A 6.64, δ_B 6.33, δ_M 5.76, δ_X 5.36, δ_Y 5.29 (J_{AB} 10, J_{AM} 14, J_{BX} 16, J_{BY} 10 Hz, N⁺CD₂-CH_M=CH_A-CH_B=CH_XH_Y), and 3.87 (s, NMe₂), with no detectable signals for C₆H₅ and NCH₂ corresponding to >99 atom % D in the phenyl group and >98 atom % D at C-1'.

Preparation of Ammonioamidates (13).*—The hydrazinium salt (12) was treated with an excess of aqueous sodium hydroxide (6M; 2 ml for each g of salt) with stirring at room temperature for 3 h. The ylide was extracted into dichloromethane and the extract dried and evaporated to give the ammonioamidate (13), as an oil in most cases. The crystalline ylides were purified by recrystallisation from hexane-di-

* These compounds are systematically named as ammonioamidates and -ureides.

chloromethane; the non-crystalline ylides were used without further purification.

N-{*Dimethyl*[(2'*E*)-*penta*-2',4'-*dienyl*]ammonio}acetamidide (13a). This was obtained as an oil (83%) (Found: M^+ , 168.1259. $C_9H_{16}N_2O$ requires M , 168.1263); ν_{\max} , 1 580 cm^{-1} ; δ 6.50–6.16 (m, CH=CH), 5.78 (dt, J 7, 14 Hz, $CH_2-CH=CH$), 5.42–5.19 (m, C=CH₂), 4.35 (d, J 7 Hz, $\overset{+}{N}CH_2$), 3.25 (s, $\overset{+}{N}Me_2$), and 1.82 (s, COCH₃).

N-{*Dimethyl*[(2'*E*)-[1',1'-²H₂]*penta*-2',4'-*dienyl*]ammonio}acetamidide (13b). This was obtained as an oil (88%) (Found: M^+ , 170.1390. $C_9H_{14}D_2N_2O$ requires M , 170.1388); ν_{\max} , 1 580 cm^{-1} ; δ 6.50–6.16 (m, CH=CH), 5.77 (d, J 14 Hz, CD_2-CH), 5.40–5.19 (m, C=CH₂), 3.25 (s, $\overset{+}{N}Me_2$), and 1.83 (s, COCH₃); a low intensity doublet for $\overset{+}{N}CH_2$ indicated ca. 97 atom % D at C-1'.

N-{*Dimethyl*[(2'*E*)-2'-*methylpenta*-2',4'-*dienyl*]ammonio}acetamidide (13c). This was obtained as a gum (78%) (Found: M^+ , 182.1419. $C_{10}H_{18}N_2O$ requires M , 182.1419); ν_{\max} , 1 575 cm^{-1} ; δ ABXY system, δ_A 6.14, δ_B 6.58, δ_X 5.27, δ_Y 5.17 (J_{AB} 10, J_{BX} 16, J_{BY} 10 Hz, =CH_A-CH_B=CH_XH_Y), 3.78 (s, $\overset{+}{N}Me_2$), 2.07 (s, COCH₃), and 1.99 (s, C=CMe).

N-{*Dimethyl*[(2'*E*)-4'-*methylpenta*-2',4'-*dienyl*]ammonio}acetamidide (13d). This was obtained as a gum (84%) (Found: M^+ , 182.1426. $C_{10}H_{18}N_2O$ requires M , 182.1419); ν_{\max} , 1 575 cm^{-1} ; δ AMX₂ system, δ_A 6.46, δ_M 5.72, δ_X 4.37 [J_{AM} 15, J_{MX} 7.5 Hz, CH_A=CH_M-C(H_X)₂], 5.10br (s, C=CH₂), 3.24 (s, $\overset{+}{N}Me_2$), 1.88 (s, C=CMe), and 1.82 (s, COCH₃).

N-{*Dimethyl*[(2'*E*)-*penta*-2',4'-*dienyl*]ammonio}ethoxyformamidide (13e). This was obtained as an oil (81%) (Found: M^+ , 198.1372. $C_{10}H_{18}N_2O_2$ requires M , 198.1368); ν_{\max} , 1 635 cm^{-1} ; δ 6.48–6.17 (m, =CH-CH=), 5.83 (dt, J 15, 7 Hz, $CH_2-CH=CH$), 5.38–5.20 (m, C=CH₂), 4.26 (d, J 7 Hz, $\overset{+}{N}CH_2$), A₂X₃ system, δ_A 3.99, δ_X 1.22 [J_{AX} 7 Hz, OC(H_A)₂-C(H_X)₃], and 3.25 (s, $\overset{+}{N}Me_2$).

N-{*Dimethyl*[(2'*E*)-[1',1'-²H₂]*penta*-2',4'-*dienyl*]ammonio}ethoxyformamidide (13f). This was obtained as an oil (75%) (Found: M^+ , 200.1495. $C_{10}H_{16}D_2N_2O_2$ requires M , 200.1493); ν_{\max} , 1 635 cm^{-1} ; δ 6.50–6.18 (m, =CH-CH=), 5.84 (d, J 15 Hz, $CD_2-CH=CH$), 5.40–5.20 (m, C=CH₂), A₂X₃ system, δ_A 4.00, δ_X 1.24 [J_{AX} 7 Hz, OC(H_A)₂C(H_X)₃], and 3.24 (s, $\overset{+}{N}Me_2$), with no detectable signal for the $\overset{+}{N}CH_2$ group consistent with >95 atom % D at C-1'.

N-{*Dimethyl*[(2'*E*)-2'-*methylpenta*-2',4'-*dienyl*]ammonio}ethoxyformamidide (13g). This was obtained as hygroscopic crystals (80%) (Found: C, 62.0; H, 9.6; N, 13.5. $C_{11}H_{20}N_2O_2$ requires C, 62.3; H, 9.4; N, 13.2%); ν_{\max} , 1 640 cm^{-1} ; δ , ABXY system, δ_A 6.56, δ_B 6.16, δ_X 5.32, δ_Y 5.28 (J_{AB} 11, J_{AX} 10, J_{AY} 16 Hz, CH_B-CH_A=CH_XH_Y), 4.31 (s, $\overset{+}{N}CH_2$), A₂X₃ system, δ_A 3.98, δ_X 1.21 [J_{AX} 7 Hz, OC(H_A)₂C(H_X)₃], 3.23 (s, $\overset{+}{N}Me_2$), and 2.00 (s, C=CMe).

N-{*Dimethyl*[(2'*E*)-4'-*methylpenta*-2',4'-*dienyl*]ammonio}ethoxyformamidide (13h). This was obtained as an oil (75%) (Found: M^+ , 212.1528. $C_{11}H_{20}N_2O_2$ requires M , 212.1525); ν_{\max} , 1 640 cm^{-1} ; δ , ABX₂ system, δ_A 6.48, δ_B 5.77, δ_X 4.31 [J_{AB} 16, J_{BX} 7 Hz, CH_A=CH_B-C(H_X)₂], 5.10br (s, C=CH₂), A₂X₃ system, δ_A 4.00, δ_X 1.23 [J_{AX} 7 Hz, OC(H_A)₂C(H_X)₃], 3.25 (s, $\overset{+}{N}Me_2$), and 1.88 (s, C=CMe).

N-{*Dimethyl*[(2'*E*)-*penta*-2',4'-*dienyl*]ammonio}methylureide (13i). This was obtained as an oil (74%) (Found: M^+ , 183.1376. $C_9H_{17}N_3O$ requires M , 183.1372); ν_{\max} , 1 590 cm^{-1} ; δ 7.50br (NHMe), 6.75–6.20 (m, =CH-CH=), 5.84 (dt, J 15, 7 Hz), 5.50–5.26 (m, C=CH₂), 4.73 (d, J 7 Hz, $\overset{+}{N}CH_2$), 3.67 (s, $\overset{+}{N}Me_2$), and 2.73 (d, J 5 Hz, MeNHCO).

N-{*Dimethyl*[(2'*E*)-[1',1'-²H₂]*penta*-2',4'-*dienyl*]ammonio}methylureide (13j). This was obtained as an oil (73%) (Found: M^+ , 185.1498. $C_9H_{15}D_2N_3O$ requires M , 185.1497); ν_{\max} , 1 590 cm^{-1} ; δ 6.77–6.22 (m, =CH-CH=), 5.84 (d, J 15 Hz, $CD_2-CH=CH$), 5.51–5.25 (m, C=CH₂), 3.71 (s, $\overset{+}{N}Me_2$), and 2.76 (d, J 5 Hz, MeNHCO), with no detectable signal for the $\overset{+}{N}CH_2$ group consistent with >95 atom % D at C-1'.

N-{*Dimethyl*[(2'*E*)-2'-*methylpenta*-2',4'-*dienyl*]ammonio}methylureide (13k). This was obtained as an oil (76%) (Found: M^+ , 197.1529. $C_{10}H_{19}N_3O$ requires M , 197.1528); ν_{\max} , 1 610 and 1 550 cm^{-1} ; δ , ABXY system, δ_A 6.58, δ_B 6.12, δ_X 5.29, δ_Y 5.25 (J_{AB} 10, J_{AX} 16, J_{AY} 10 Hz, CH_B-CH_A=CH_XH_Y), 4.35 (s, $\overset{+}{N}CH_2$), 3.25 (s, $\overset{+}{N}Me_2$), 2.66 (d, J 5 Hz, MeNCHO), and 2.00 (s, C=CMe).

N-{*Dimethyl*[(2'*E*)-4'-*methylpenta*-2',4'-*dienyl*]ammonio}methylureide (13l). This was obtained as an oil (70%) (Found: M^+ , 197.1525. $C_9H_{19}N_3O$ requires M , 197.1528); ν_{\max} , 1 595 cm^{-1} ; δ , ABX₂ system, δ_A 6.44, δ_B 5.76, δ_X 4.34 [J_{AB} 16, J_{BX} 7 Hz, CH_A=CH_B-C(H_X)₂], 5.06 (s, C=CH₂), 3.26 (s, $\overset{+}{N}Me_2$), 2.66 (d, J 5 Hz, MeNHCO), and 1.87 (s, C=CMe).

N-{*Dimethyl*[(2'*E*)-2'-*methylpenta*-2',4'-*dienyl*]ammonio}phenylureide (13m). This was obtained as crystals (89%), m.p. 95–97 °C (Found: C, 69.2; H, 8.1; N, 16.5. $C_{15}H_{21}N_3O$ requires C, 69.5; H, 8.1; N, 16.2%); ν_{\max} , 1 625 and 1 590 cm^{-1} ; δ 7.40–7.08 (m, 5 aryl H), ABXY system, δ_A 6.53, δ_B 6.14, δ_X 5.30, δ_Y 5.25 (J_{AB} 10, J_{AX} 16, J_{AY} 10 Hz, =CH_B-CH_A=CH_XH_Y), 4.37 (s, $\overset{+}{N}CH_2$), 3.24 (s, $\overset{+}{N}Me_2$), and 2.00 (s, C=CMe).

N-{*Dimethyl*[(2'*E*)-4'-*methylpenta*-2',4'-*dienyl*]ammonio}phenylureide (13n). This was obtained as crystals (94%), m.p. 111–113 °C (Found: C, 69.2; H, 8.3; N, 16.5. $C_{15}H_{21}N_3O$ requires C, 69.5; H, 8.1; N, 16.2%); ν_{\max} , 1 625 and 1 590 cm^{-1} ; δ 7.39–6.74 (m, 5 aryl H), ABX₂ system, δ_A 6.45, δ_B 5.78, δ_X 4.34 [J_{AB} 16, J_{BX} 7 Hz, CH_A=CH_B-C(H_X)₂], 5.08br (s, C=CH₂), 3.27 (s, $\overset{+}{N}Me_2$), and 1.86 (s, C=CMe).

N-{*Dimethyl*[(2'*E*)-*penta*-2',4'-*dienyl*]ammonio}benzamidide (13o). This was obtained as an oil (92%) (Found: M^+ , 230. $C_{14}H_{18}N_2O$ requires M , 230); ν_{\max} , 1 600, 1 565, and 1 558 cm^{-1} ; δ 8.00–7.84 (m, 2 *ortho*-H of C₆H₅), 7.40–7.20 (m, 3 aryl H), 6.50–6.22 (m, =CH-CH=), 5.50 (dt, J 15, 7 Hz, CH=CH-CH₂), 5.43–5.08 (m, C=CH₂), 4.37 (d, J 7 Hz, $\overset{+}{N}CH_2$), and 3.41 (s, $\overset{+}{N}Me_2$).

N-{*Dimethyl*[(2'*E*)-[1',1'-²H₂]*penta*-2',4'-*dienyl*]ammonio}[²H₅]benzamidide (13p). This was obtained as an oil (94%) (Found: C, 70.8; H, 7.9; N, 11.85. $C_{14}H_{11}D_5N_2O$ requires C, 70.9; H, 7.6; N, 11.8%); ν_{\max} , 1 580 and 1 535 cm^{-1} ; δ 6.50–6.30 (m, =CH-CH), 5.84 (d, J 15 Hz, CH=CH-CD₂), 5.50–5.15 (m, C=CH₂), and 3.36 (s, $\overset{+}{N}Me_2$), with no detectable signal for the C₆H₅ group and a low intensity signal for $\overset{+}{N}CH_2$ indicating ca. 95 atom % D at C-1'.

Thermal Rearrangement of Ammonioamidates (13).—The ylide (500 mg) was heated in dry benzene under the conditions specified in Table 1. The product mixtures were separated by preparative t.l.c. on silica. Individual rearrangement products were characterised as indicated below.

N-{*Dimethyl*[(2'*E*)-*penta*-2',4'-*dienyl*]ammonio}acetamidide (13a). This gave 2-acetyl-1,1-dimethyl-2-[(2'*E*)-*penta*-2',4'-*dienyl*]hydrazine (14a) as an oil (440 mg) which was purified by distillation at 160–162 °C/0.1 mmHg (Found: C, 64.2; H, 9.3; N, 16.8. $C_9H_{16}N_2O$ requires C, 64.3; H, 9.5; N, 16.7%); ν_{\max} , 1 685, 1 600, and 1 585 cm^{-1} ; δ 6.47–6.03 (m, =CH-CH=), 5.77 (dt, J 14, 6 Hz, CH=CH-CH₂), 5.25–4.98 (m, C=CH₂), 3.99 (d, J 6 Hz, NCH₂), 2.56 (s, NMe₂), and 1.15 (s, COCH₃).

N-{*Dimethyl*[(2'E)-[1',1'-²H₂]penta-2',4'-dienyl]ammonio}-acetamide (13b). This gave a 1:1 mixture of the [1',1'-²H₂]hydrazine derivative (14b) and the [5',5'-²H₂]hydrazine derivative (15b) as a liquid, b.p. 160–165 °C/0.1 mmHg (Found: *M*⁺, 170. C₉H₁₄D₂N₂O requires *M*, 170). The distribution of deuterium between positions 1' and 5' of the pentadienyl substituent was determined by integration of the n.m.r. spectrum of the 1'-H₂ and 5'-H₂ signals (δ 4.01 and δ 5.26–4.96 respectively).

N-{*Dimethyl*[(2'E)-2'-methylpenta-2',4'-dienyl]ammonio}-acetamide (13c). This gave a 1:2 mixture of the 2'-methylpentadienylhydrazine (14c) and the 4'-methylpentadienylhydrazine (15c) which could not be separated into its two components (Found: *M*⁺, 182.1426. C₁₀H₁₈N₂O requires *M*, 182.1419); *v*_{max.} 1 650 cm⁻¹; δ(2'-methylpentadienylhydrazine) ABXY system, δ_A 5.89, δ_B 6.54, δ_X 5.12, δ_Y 5.04 (*J*_{AB} 10, *J*_{BX} 16, *J*_{BY} 10 Hz, =CH_A-CH_B=CH_XH_Y), 4.05 (s, NCH₂), 2.55 (s, NMe₂), 2.20 (s, COCH₃), and 1.80 (s, C=CMe); δ(4'-methylpentadienylhydrazine) ABX₂ system, δ_A 6.26, δ_B 5.72, δ_X 4.05 [*J*_{AB} 16, *J*_{BX} 5 Hz, CH_A=CH_B-C(H_X)₂], 4.93 (s, C=CH₂), 2.55 (s, NMe₂), 2.15 (s, COCH₃), and 1.80 (s, C=CMe). The composition of the mixture was based upon the integrated intensities of the COCH₃ signals (δ 2.20 and 2.15).

N-{*Dimethyl*[(2'E)-4'-methylpenta-2',4'-dienyl]ammonio}-acetamide (13d). This gave a mixture of the 2'-methylpentadienylhydrazine [(15d) ≡ (14c)] and the 4'-methylpentadienylhydrazine [(14d) ≡ (15c)] in the same ratio (1:2) as the 2'-methylpentadienylammonioamide (13c).

N-{*Dimethyl*[(2'E)-penta-2',4'-dienyl]ammonio}ethoxyformamide (13e). This gave two products. (a) 2-Ethoxycarbonyl-1,1-dimethyl-2-[(2'E)-penta-2',4'-dienyl]hydrazine (14e) (380 mg) as a liquid, b.p. 120–125 °C/12 mmHg (Found: C, 60.3; H, 8.9; N, 14.1. C₁₀H₁₈N₂O₂ requires C, 60.6; H, 9.1; N, 14.1%). *v*_{max.} 1 685 and 1 604 cm⁻¹; δ 6.52–6.02 (m, =CH-CH=), 5.73 (dt, *J* 13, 6 Hz, CH=CH-CH₂), 5.28–4.98 (m, C=CH₂), A₂X₃ system, δ_A 4.17, δ_X 1.27 [*J*_{AX} 7 Hz, OC(H_A)₂C(H_X)₃], 3.94 (d, *J* 6 Hz, NCH₂), and 2.67 (s, NMe₂).

(b) 2-Ethoxycarbonyl-1,1-dimethyl-2-(penta-1',4'-dien-3'-yl)hydrazine (16e) (63 mg) as a liquid (Found: *M*⁺, 198.1370. C₁₀H₁₈N₂O₂ requires *M*, 198.1368), *v*_{max.} (pure liquid) 1 700 and 1 640 cm⁻¹; δ, AA'XX'YY'Z system, δ_A = δ_{A'} 6.02, δ_X = δ_{X'} 5.19, δ_Y = δ_{Y'} 5.17, δ_Z 4.92 (*J*_{AX} = *J*_{A'X'} 16, *J*_{AY} = *J*_{A'Y'} 9.5, *J*_{AZ} = *J*_{A'Z} 6.5 Hz, CH_XH_Y=CH_A-CH_Z-CH_{A'}=CH_{X'}H_{Y'}), A₂X₃ system, δ_A 4.19, δ_X 1.29 [*J*_{AX} 7 Hz, OC(H_A)₂C(H_X)₃], and 2.71 (s, NMe₂).

N-{*Dimethyl*[(2'E)-[1',1'-²H₂]penta-2',4'-dienyl]ammonio}ethoxyformamide (13f). This gave two products. (a) A 1:1 mixture of the [1',1'-²H₂]hydrazine derivative (14f) and the [5',5'-²H₂]hydrazine derivative (15f) as a liquid, b.p. 120–130 °C/12 mmHg (Found: *M*⁺, 200. C₁₀H₁₆D₂N₂O₂ requires *M*, 200). The deuterium distribution between positions 1' and 5' of the pentadienyl substituent was determined by integration of the n.m.r. spectrum of the 1'-H₂ and 5'-H₂ signals (δ 3.96 and δ 5.30–4.99 respectively).

(b) The [1',1'-²H₂]hydrazine derivative (16f) as a liquid (Found: *M*⁺, 200. C₁₀H₁₆D₂N₂O₂ requires *M*, 200).

N-{*Dimethyl*[(2'E)-2'-methylpenta-2',4'-dienyl]ammonio}ethoxyformamide (13g). This gave three products.

(a) 2-Ethoxycarbonyl-1,1-dimethyl-2-[(2'E)-2'-methylpenta-2',4'-dienyl]hydrazine (14g) was obtained as a liquid, b.p. 110 °C/0.05 mmHg (130 mg) (Found: C, 62.1; H, 9.3; N, 13.5. C₁₁H₂₀N₂O₂ requires C, 62.3; H, 9.4; N, 13.2%); *v*_{max.} 1 680 and 1 595 cm⁻¹; δ, ABXY system, δ_A 6.54, δ_B 5.95, δ_X 5.13, δ_Y 5.03 (*J*_{AB} 10, *J*_{AX} 16, *J*_{AY} 10 Hz, =CH_B-CH_A=CH_XH_Y), A₂X₃ system, δ_A 4.15, δ_X 1.25 [*J*_{AX} 7 Hz, OC(H_A)₂C(H_X)₃], 3.86 (s, NCH₂), 2.65 (s, NMe₂), and 1.75 (s, C=CMe).

(b) 2-Ethoxycarbonyl-1,1-dimethyl-2-[(2'E)-4'-methylpenta-2',4'-dienyl]hydrazine (15g) was obtained as a liquid, b.p. 120–122 °C/0.05 mmHg (265 mg) (Found: C, 62.1; H, 9.3; N, 13.4. C₁₁H₂₀N₂O₂ requires C, 62.3; H, 9.4; N, 13.2%); *v*_{max.} 1 680 and 1 602 cm⁻¹; δ, ABX₂ system, δ_A 6.26, δ_B 5.65, δ_X 3.95 [*J*_{AB} 16, *J*_{AX} 7 Hz, CH_A=CH_B-C(H_X)₂], 4.92 (s, C=CH₂), A₂X₃ system, δ_A 4.16, δ_X 1.26 [*J*_{AX} 7 Hz, OC(H_A)₂C(H_X)₃], 2.66 (s, NMe₂), and 1.82 (s, C=CMe).

(c) 2-Ethoxycarbonyl-1,1-dimethyl-2-(2'-methylpenta-1',4'-dien-3'-yl)hydrazine (16g) was obtained as a liquid (65 mg) (Found: *M*⁺, 212.1526. C₁₁H₂₀N₂O₂ requires *M*, 212.1525); δ, AMNX system, δ_A 6.19, δ_M 5.18, δ_N 5.16, δ_X 4.76 (*J*_{AM} 18, *J*_{AN} 9, *J*_{AX} 10 Hz, CH_X-CH_A=CH_MH_N), 4.92 (s, C=CH₂), A₂X₃ system, δ_A 4.18, δ_X 1.27 [*J*_{AX} 7 Hz, OC(H_A)₂C(H_X)₃], 2.66 (s, NMe₂), and 1.77 (s, C=CMe).

N-{*Dimethyl*[(2'E)-4'-methylpenta-2',4'-dienyl]ammonio}ethoxyformamide (13h). This gave the 2'-methylpentadienylhydrazine [(15h) ≡ (14g)] (153 mg), the 4'-methylpentadienylhydrazine [(14h) ≡ (15g)] (296 mg), and the 2'-methylpenta-1',4'-dien-3'-ylhydrazine [(16h) ≡ (16g)] (123 mg).

N-{*Dimethyl*[(2'E)-penta-2',4'-dienyl]ammonio}methylureide (13i) gave two products.

(a) 1,1-Dimethyl-2-methylcarbamoyl-2-[(2'E)-penta-2',4'-dienyl]hydrazine (14i) (345 mg) was obtained as a liquid, b.p. 130–135 °C/0.01 mmHg (Found: *M*⁺, 183.1370. C₉H₁₇N₃O requires *M*, 183.1372); *v*_{max.} 3 420 and 1 648 cm⁻¹; δ 6.48–6.04 (m, =CH-CH=), 5.80 (dt, *J* 15, 6 Hz, CH=CH-CH₂), 5.20–4.90 (m, C=CH₂), 3.98 (d, *J* 6 Hz, NCH₂), 2.78 (d, *J* 5 Hz, CONHMe), and 2.48 (s, NMe₂).

(b) 1,1-Dimethyl-2-methylcarbamoyl-2-(penta-1',4'-dien-3'-yl)hydrazine (16i) (120 mg) was obtained as crystals, m.p. 65–66 °C (Found: C, 59.3; H, 9.1; N, 22.9. C₉H₁₇N₃O requires C, 59.0; H, 9.3; N, 22.95%); *v*_{max.} 3 420 and 1 650 cm⁻¹; δ, AA'MM'NN'X system, δ_A = δ_{A'} 6.31, δ_M = δ_{M'} 5.13, δ_N = δ_{N'} 5.12, δ_X 4.33 (*J*_{AM} = *J*_{A'M'} 17.5, *J*_{AN} = *J*_{A'N'} 9.5, *J*_{AX} = *J*_{A'X} 7 Hz, CH_MH_N=CH_A-CH_X-CH_{A'}=CH_{M'}H_{N'}), 1.78 (d, *J* 5 Hz, CONHMe), and 1.55 (s, NMe₂).

N-{*Dimethyl*[(2'E)-[1',1'-²H₂]penta-2',4'-dienyl]ammonio}methylureide (13j). This gave two products.

(a) A 1:1 mixture of the [1',1'-²H₂]hydrazine derivative (14j) and the [5',5'-²H₂]hydrazine derivative (15j) as a liquid, b.p. 130–135 °C/0.01 mmHg (Found: *M*⁺, 185. C₉H₁₅D₂N₃O requires *M*, 185). The deuterium distribution between positions 1' and 5' of the pentadienyl substituent was determined by integration of the C(1')H₂ and C(5')H₂ signals (δ 3.98 and δ 5.20–4.90 respectively).

(b) The [1',1'-²H₂]hydrazine derivative (16j) as crystals, m.p. 64–65 °C (Found: C, 58.9; H, 9.1; N, 22.7%; *M*⁺, 185. C₉H₁₅D₂N₃O requires C, 58.4; H, 9.2; N, 22.7%; *M*, 185).

N-{*Dimethyl*[(2'E)-2'-methylpenta-2',4'-dienyl]ammonio}methylureide (13k). This gave three products.

(a) 1,1-Dimethyl-2-methylcarbamoyl-2-[(2'E)-2'-methylpenta-2',4'-dienyl]hydrazine (14k) was obtained as an oil, b.p. 115–120 °C/0.02 mmHg (Found: C, 60.2; H, 9.7; N, 21.3. C₁₀H₁₉N₃O requires C, 60.9; H, 9.7; N, 21.3%); *v*_{max.} 3 420, 1 650, and 1 525 cm⁻¹; δ, ABXY system, δ_A 6.57, δ_B 5.97, δ_X 5.11, δ_Y 5.05 (*J*_{AB} 10, *J*_{AX} 17, *J*_{AY} 10 Hz, =CH_B-CH_A=CH_XH_Y), 4.03 (s, NCH₂), 2.82 (d, *J* 5 Hz, CONHMe), 2.50 (s, NMe₂), and 1.81 (s, C=CMe).

(b) 1,1-Dimethyl-2-methylcarbamoyl-2-[(2'E)-4'-methylpenta-2',4'-dienyl]hydrazine (15k) was obtained as an oil, b.p. 115–120 °C/0.02 mmHg (Found: C, 60.7; H, 9.8; N, 21.5. C₁₀H₁₉N₃O requires C, 60.9; H, 9.7; N, 21.3%); *v*_{max.} 3 420, 1 648, and 1 528 cm⁻¹; δ, ABX₂ system, δ_A 6.29, δ_B 5.77, δ_X 4.07 [*J*_{AB} 16, *J*_{BX} 6 Hz, CH_A=CH_B-C(H_X)₂], 4.72 (s, C=CH₂), 2.82 (d, *J* 5 Hz, CONHMe), 2.50 (s, NMe₂), and 1.81 (s, C=CMe). The hydrazines (9k) and (10k) were obtained in a 1:2 ratio (356 mg) on the basis of g.c. analysis.

(c) 1,1-Dimethyl-2-methylcarbamoyl-2-(2'-methylpenta-1',4'-dien-3'-yl)hydrazine (16k) was obtained as crystals (95 mg), m.p. 60–61 °C (Found: C, 60.7; H, 9.7; N, 21.1). $C_{10}H_{19}N_3O$ requires C, 60.9; H, 9.7; N, 21.3%; ν_{\max} , 3 420, 1 651, and 1 510 cm^{-1} ; δ AMNX system, δ_A 6.42, δ_M 5.18, δ_N 5.11, δ_X 4.19 (J_{AM} 10, J_{AN} 18, J_{AX} 8 Hz, $CH_XCH_A=CH_MH_N$), 4.90 (s, $C=CH_2$), 2.75 (d, J 5 Hz, $CONHMe$), 2.51 (s, NMe_2), and 1.77 (s, $C=CMe$).

N-{Dimethyl[(2'E)-4'-methylpenta-2',4'-dienyl]ammonio}-methylureide (13l). This gave the 2'-methylpentadienylhydrazine [(15l) \equiv (14k)] and the 4'-methylpentadienylhydrazine [(14l) \equiv (15k)] (280 mg) in a 1 : 2 ratio, and the 3'-(2'-methylpenta-1',4'-dienyl)hydrazine (180 mg) [(16l) \equiv (16k)].

N-{Dimethyl[(2'E)-2'-methylpenta-2',4'-dienyl]ammonio}-phenylureide (13m). This gave three products.

(a) A mixture of 1,1-dimethyl-2-[(2'E)-2'-methylpenta-2',4'-dienyl]-2-phenylcarbamoylhydrazine (14m) and 1,1-dimethyl-2-[(2'E)-4'-methylpenta-2',4'-dienyl]-2-phenylcarbamoylhydrazine (15m) (1 : 2 ratio) was obtained as a viscous oil (373 mg) which could not be separated into its components by t.l.c. or g.c. (Found: M^+ , 259. $C_{15}H_{21}N_3O$ requires M , 259); ν_{\max} , 3 325, 1 665, 1 600, and 1 590 cm^{-1} ; for the hydrazine (14m): δ , 8.67br (s NH), 7.54–6.82 (m, 5 aryl H), ABXY system, δ_A 6.54, δ_B 5.95, δ_X 5.10, δ_Y 5.00 (J_{AB} 10, J_{AX} 16, J_{AY} 10 Hz, $=CH_B-CH_A=CH_XH_Y$), 4.05 (s, NCH_2), 2.55 (s, NMe_2), and 1.80 (s, $C=CMe$); for the hydrazine (15m): δ , 8.54br (s, NH), 7.54–6.82 (m, 5 aryl H), ABX₂ system, δ_A 6.27, δ_B 5.75, δ_X 4.07 [J_{AB} 15, J_{BX} 6 Hz, $CH_A=CH_B-C(H_X)_2$], 4.90 (s, $C=CH_2$), 2.55 (s, NMe_2), and 1.80 (s, $C=CMe$).

(b) 1,1-Dimethyl-2-(2'-methylpenta-1',4'-dien-3'-yl)-2-phenylcarbamoylhydrazine (16m) was obtained as crystals, m.p. 77–78 °C (87 mg) (Found: C, 69.6; H, 8.3; N, 16.2). $C_{15}H_{21}N_3O$ requires C, 69.5; H, 8.1; N, 16.2%; ν_{\max} , 3 360, 1 685, 1 608, and 1 595 cm^{-1} ; δ , 8.57br (s, NH), 7.57–6.90 (m, 5 aryl H), AMNX system, δ_A 6.45, δ_M 5.22, δ_N 5.16, δ_X 4.15 (J_{AM} 18, J_{AN} 10, J_{AX} 8 Hz, $CH_X-CH_A=CH_MH_N$), 4.94 (s, $C=CH_2$), 2.60 (s, NMe_2), and 1.80 (s, $C=CMe$).

N-{Dimethyl[(2'E)-4'-methylpenta-2',4'-dienyl]ammonio}-phenylureide (13n). This gave a mixture of the 2'-methylpentadienylhydrazine [(15n) \equiv (14m)] and the 4'-methylpentadienylhydrazine [(14n) \equiv (15m)] (1 : 2 ratio, 345 mg) and the 2'-methylpenta-1',4'-dien-3'-ylhydrazine [(16n) \equiv (16m)] (23%). The hydrazine (16n) rearranged when heated in xylene at 138–140 °C for 20 h. The products were separated by t.l.c. to give a 1 : 2 mixture of the hydrazines (15n) and (14n) (60%) and unchanged hydrazine (16n) (20%).

N-{Dimethyl[(2'E)-penta-2',4'-dienyl]ammonio}benzamide (13o). This gave 2-benzoyl-1,1-dimethyl-2-[(2'E)-penta-2',4'-dienyl]hydrazine (14o) as an oil, b.p. 145–150 °C/0.02 mmHg (460 mg) (Found: C, 72.7; H, 8.1; N, 11.9. $C_{14}H_{18}N_2O$ requires C, 73.0; H, 7.8; N, 12.2%); ν_{\max} (neat liquid) 1 645, 1 605, and 1 580 cm^{-1} ; δ 7.60–7.20 (m, 5 aryl H), 6.54–6.08 (m, $=CH-CH=$), 6.02–5.72 (m, $CH=CH-CH_2$), 5.32–4.98 (m, $C=CH_2$), 4.11 (d, J 6 Hz, NCH_2), and 2.51 (s, NMe_2).

Thermal Rearrangement of N-{Dimethyl[(2'E)-penta-2',4'-dienyl]ammonio}benzamide (13o).—(a) *Determination of intramolecularity.* The rearrangement of a 1 : 1 mixture of the [2H_0]ammonioamidate (13o) and the [2H_7]ammonioamidate (13p) (0.001 mol) in the specified solvent (5 ml) was carried out under the conditions summarised in Table 2. The reaction mixture was diluted with ether (75 ml) and water (20 ml). The organic layer was separated and evaporated and the residual oil dissolved in hydrochloric acid (20 ml; 10%); the acidic solution was washed with ether, made basic (10% aqueous NaOH), and extracted with ether. The ether extract was evaporated to give the rearrangement product (14o) which

was purified by t.l.c. The isotopic composition of the product was determined by mass spectral analysis, based upon peak heights (averaged over several spectra) of the M^+ , $(M-2)^+$, $(M+5)^+$, and $(M+7)^+$ ions.

(b) *Determination of relative amounts of 1',2 and 5',2 coupling.* The rearrangement of the [2H_7]ammonioamidate (13p) (0.001 mol) was carried out under the conditions summarised in Table 2. The [2H_7]hydrazine derivative [(14p) \div (15p)] was isolated, and the distribution of deuterium between positions 1' and 5' determined by comparison of the intensities of the n.m.r. signals (δ 4.11 and δ 5.32–4.93) corresponding to 1'-H₂ and 5'-H₂.

Measurement of Penta-1',5'-dienyl Scrambling in Ammonioamidates (13).—The ammonioamidate (13) in benzene (15 ml) was heated at the temperatures indicated in Table 3. Samples (1 ml) were removed at measured time intervals and evaporated at room temperature to give a mixture of recovered ylide and rearrangement products. The composition of this mixture was determined by n.m.r. analysis as outlined below.

N-{Dimethyl[(2'E)-[1',1'- 2H_2]penta-2',4'-dienyl]ammonio}-[2H_5]benzamide (13p). 1',5'-Scrambling of the pentadienyl group of the ylide was followed from the increasing intensity of the NCH_2 signal (d, δ 4.36). The rate of rearrangement was followed by the decreasing intensity of the NMe_2 signal (s, δ 3.30) of the ylide and the increasing intensity of the NMe_2 signal (s, δ 2.49) of the rearrangement products (14p) \div (15p).

N-{Dimethyl[(2'E)-[1',1'- 2H_2]penta-2',4'-dienyl]ammonio}-ethoxyformamide (13f). 1',5'-Scrambling was followed by the increasing intensity of the NCH_2 signal (d, δ 4.26) of the ylide, isolated from the reaction products by preparative t.l.c. (chloroform-methanol, 9 : 1). The rate of rearrangement was followed by the decreasing intensity of the NMe_2 signal (s, δ 3.24) of the ylide and the increasing intensity of the NMe_2 signal (s, δ 2.61) of the rearrangement products (14f) \div (15f) + (16f).

N-{Dimethyl[(2'E)-2'-methylpenta-2',4'-dienyl]ammonio}-acetamide (13c). 1',5'-Scrambling was followed by the decreasing intensity of the $COCH_3$ signal (s, δ 1.99) of the ylide (13c) and the increasing intensity of the $COCH_3$ signal (s, δ 1.88) of the ylide (13d). The rate of rearrangement was determined from the decreasing intensity of the NMe_2 signal (s, δ 3.25) of the ylides (13c) and (13d) and the increasing intensity of the NMe_2 signal (s, δ 2.52) of the rearrangement products (14c) + (15c).

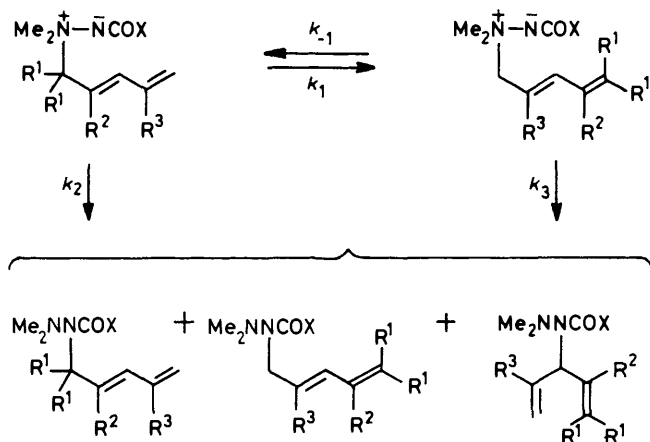
N-{Dimethyl[(2'E)-2'-methylpenta-2',4'-dienyl]ammonio}-ethoxyformamide (13g). 1',5'-Scrambling was followed by the decreasing intensity of the $C=CMe$ signal (s, δ 2.00) of the ylide (13g) and the increasing intensity of the $C=CMe$ signal (s, δ 1.88) of the ylide (13h). The rate of rearrangement was determined from the decreasing intensity of the NMe_2 signal (s, δ 3.23) of the ylides (13g) and (13h) and the increasing intensity of the NMe_2 signal (s, δ 2.65) of the products (14g) + (15g) + (16g).

N-{Dimethyl[(2'E)-2'-methylpenta-2',4'-dienyl]ammonio}-methylureide (13k). 1',5'-Scrambling was followed by the decreasing intensity of the $C=CMe$ signal (s, δ 2.00) of the ylide (13k) and the increasing intensity of the $C=CMe$ signal (s, δ 1.87) of the ylide (13l). The rate of rearrangement was determined from the decreasing intensity of the NMe_2 signal (s, δ 3.25) of the ylides (13k) and (13l) and the increasing intensity of the NMe_2 signals (s, δ 2.51 and s, δ 2.47) of the products (14k) + (15k) + (16k).

Table 3. Rates of competing 1',5'-scrambling and rearrangements of the ylides (13c), (13f), (13g), (13k), (13m), and (13p) in benzene

Ylide (13)	R ¹	R ²	R ³	X	Temp. (°C)	Reaction rates (s ⁻¹ × 10 ⁶)			
						k ₁	k ₋₁	k ₂	k ₃
(13c)	H	Me	H	Me	80	60	a	150	20
(13f)	D	H	H	OEt	80	20 ^b	20 ^b	150 ^b	150 ^b
(13g)	H	Me	H	OEt	80	500	a	1 600	180
(13k)	H	Me	H	NHMe	60	2 000	a	6 000	220
(13m)	H	Me	H	NHPh	40	200	a	80	1
(13p)	D	H	H	C ₆ D ₅	80	5 ^b	5 ^b	17 ^b	17 ^b

^a Not obtainable from data, assumed to be 0.01 k₁ since signals assignable to 2'-methylpenta-2',4'-dienyl ylides are not detectable after completed 1',5'-scrambling. ^b For [1',1'-²H₂]ylides assumed: k₁ = k₋₁ and k₂ = k₃.



Scheme 3. Competing 1',5'-scrambling and rearrangement of ylides (13)

N-{Dimethyl[(2'E)-2'-methylpenta-2',4'-dienyl]ammonio}-phenylureide (13m). 1',5'-Scrambling was followed by the decreasing intensity of the C=CMe signal (s, δ 2.00) of the ylide (13m) and the increasing intensity of the C=CMe signal (s, δ 1.86) of the ylide (13n). The rate of rearrangement was determined from the decreasing intensity of the NMe₂ signal (s, δ 3.24) of the ylides (13m) and (13n) and the increasing intensity of the NMe₂ signals (s, δ 2.61 and s, δ 2.55) of the products (14m) + (15m) + (16m).

Determination of Rates of Penta-1',5'-dienyl Scrambling and Rates of Rearrangement for the Ylides (13c), (13f), (13g), (13k), (13m) and (13p).—The above data for the composition of reactants at measured times were compared with computed

compositions for selected input values of rates, *k*, *k*₋₁, *k*₂, and *k*₃ in the reaction scheme outlined below (Scheme 3). The computation was based upon equations given in ref. 11.

Values of *k*₁, *k*₋₁, *k*₂ and *k*₃ obtained in this way are of limited accuracy due to the inaccuracy of n.m.r. integration (estimated error ±10% of measured value).

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