# The Thermal Rearrangement of 1-Substituted 1*H*-Azepines to Derivatives of 6-Aminofulvene

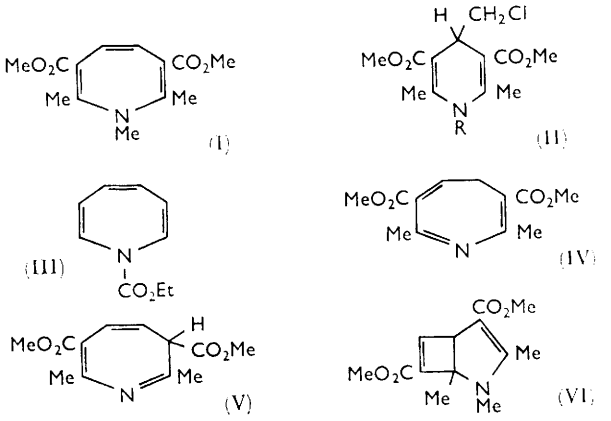
By **R. F. Childs, R. Grigg, and A. W. Johnson,** The University, Nottingham

Rearrangement with the formation of dimethyl 3,α-dimethyl-6-methylaminofulvene-2,4-dicarboxylate occurs readily when dimethyl 1,2,7-trimethyl-1*H*-azepine-3,6-dicarboxylate is heated under reflux in benzene, or when dimethyl 4-chloromethyl-1,4-dihydro-1,2,6-trimethylpyridine-3,5-dicarboxylate is heated in mesitylene in the presence of barium carbonate. Other examples of this rearrangement are described and the structures of the fulvenes are supported by the interpretation of their mass spectral fragmentation patterns. 2,4-Diacetyl-α-hydroxy-3,α-dimethylfulvene is formed by the acid hydrolysis of the rearrangement product of 3,5-diacetyl-4-chloromethyl-1,4-dihydro-1,2,6-trimethylpyridine and has also been prepared by the progressive acetylation of sodium methylcyclopentadienide.

We have described the preparation and some of the properties of dimethyl 1,2,7-trimethyl-1*H*-azepine-3,6-dicarboxylate (I),[1] which was obtained from the *N*-methyl-1,4-dihydropyridine ester (II; R = Me) by treatment with potassium t-butoxide. One of the most interesting reactions of (I) is the almost quantitative rearrangement

[1] R. F. Childs and A. W. Johnson, *J. Chem. Soc.* (*C*), 1966, 1950.

it undergoes when it is heated under mild conditions, for example in benzene heated under reflux, and this reaction forms the subject of the present Paper.




Many of the azepines already described in the literature are known to undergo thermal rearrangements. Thus, when 1-ethoxycarbonylazepine (III) is heated, it gives ethyl *N*-phenylcarbamate [2] and we have described [3] the conversion of the 4*H*-azepine (IV) to the 3*H*-azepine (V). However, the latter rearrangement required (IV) to be heated to *ca.* 300°, which is in marked contrast to the mild conditions required for the rearrangement of (I). Although the *N*-methylazepine (I) can be sublimed unchanged at 80°/1 mm., the rearrangement is also effected when (I) is passed through a tube containing fine sand, and preheated at 130°. Similar treatment of the valence tautomer (VI) [1] of the azepine gave the same rearrangement product, as did the parent dihydropyridine ester (II; R = Me) when it was heated under reflux in mesitylene in the presence of barium carbonate for 4—6 hr.

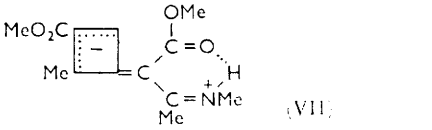
The thermolysis product, $C_{13}H_{17}NO_4$, was not obtained from (I) by a simple hydride shift, and it did not contain a benzene ring. Although analysis and nuclear magnetic resonance (n.m.r.) measurements showed the presence of two methoxycarbonyl groups, careful measurement of the intensity of the infrared band at 1710 cm.$^{-1}$ ($\varepsilon_{max.}$ 555) and comparison with several cyclic αβ-unsaturated esters of a somewhat related type, showed that this band corresponded to only one of the ester groups. As there was no other absorption in the carbonyl region above 1640 cm.$^{-1}$, it was concluded that the second ester carbonyl absorption was in the same region as the C=C stretching frequencies and that this αβ-unsaturated ester grouping was very strongly hydrogen bonded. The hydrogen bonding also involved an NH group; although there was no infrared band above 3000 cm.$^{-1}$ corresponding to NH, the presence of a proton attached to the nitrogen atom was revealed by the n.m.r. spectrum where it appeared as a broad band at τ −3. The imino-proton could also be exchanged with deuterium. A doublet at τ 6·84 ($J$ = 5·5 c./sec.) in the n.m.r. spectrum of the thermolysis product was associated with a methyl group also attached to the imino-nitrogen atom and coupled with the imino-proton, *i.e.*, indicating the presence of −NHMe. The above coupling constant was the same as is observed for the *N*-methyl group of methyl β-methylaminocrotonate, MeC(NHMe):CH·$CO_2$Me. The low-field position of the NH signal compared with those of other strongly bonded uncharged imino-groups, for example, that of methyl β-methylaminocrotonate, which shows the corresponding signal at τ 1·5, led us to suspect that there was a whole or partial positive charge on the nitrogen atom. The overall neutral character of the molecule (ease of sublimation; chromatographic behaviour) favoured an ylid type structure. The n.m.r. spectrum also revealed the presence of two unsplit *C*-methyl groups and one nuclear proton. The most noteworthy chemical property of the thermolysis product was the ease with which the methyliminium grouping could be replaced by hydroxonium (=$\overset{+}{O}$H). This occurred readily when it was warmed with dilute aqueous potassium hydroxide; after acidification a crystalline hydrolysis product was obtained in which the only change in the molecule was =$\overset{+}{N}$HMe ⟶ =$\overset{+}{O}$H. Spectroscopically, this alkaline hydrolysis product was similar to the thermolysis product. The infrared spectrum contained no identifiable OH stretching frequency and one ester carbonyl stretching frequency was again very low due to hydrogen bonding. The hydroxyl proton, which could be exchanged with deuterium, corresponded in the n.m.r. spectrum to a sharp singlet at τ −6·48, which suggested that the oxygen atom was electron deficient (*i.e.*, C=$\overset{+}{O}$H). The product readily dissolved in dilute aqueous potassium hydroxide and was reprecipitated on subsequent acidification, thus confirming its acidic nature. When the hydrolysis product was heated with methanolic ammonia, or with a variety of primary or secondary amines, similar nucleophilic displacements occurred (=$\overset{+}{O}$H ⟶ =$\overset{+}{N}$RR′; R = R′ = H or Me; R = H, R′ = Me, *p*-$C_6H_4Cl$, or $C_6H_5$). The product derived from methylamine was identical with the initial thermolysis product of (I). In the case of the product derived from dimethylamine (=$\overset{+}{N}Me_2$), the strong diminution of the ester carbonyl frequency was not observed, *i.e.*, hydrogen bonding did not occur in this case as there was no proton attached to the nitrogen atom.

Mild treatment of the thermolysis product with acid again caused replacement of the methyliminium group by =$\overset{+}{O}$H, but in addition the non-bonded ester was eliminated by hydrolysis and decarboxylation. The crystalline acid hydrolysis product could be aminated (=$\overset{+}{O}$H ⟶ =$\overset{+}{N}$RR′) in the same way as the alkaline hydrolysis product (above).

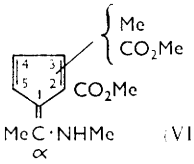
In a preliminary Communication,[4] we suggested that the thermolysis product and its derivatives contained

[2] K. Hafner, *Angew. Chem., Internat. Edn.*, 1964, **3**, 165.
[3] M. Anderson and A. W. Johnson, *J. Chem. Soc.*, 1965, 2411.
[4] R. F. Childs and A. W. Johnson, *Chem. Comm.*, 1965, 95.

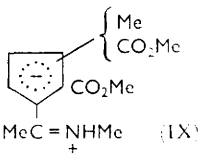
four-membered rings, *e.g.*, (VII), which could be derived from (VI) by fission of the five-membered ring without an extensive rearrangement. However, it was realised that such structures were resonance hybrids of cyclobutadienes and the stability of the products was the more remarkable. As a result of the interpretation of the mass spectral fragmentation patterns and further chemical work, it is now necessary to amend the earlier formulation, and the compounds are now regarded as fulvene derivatives. Thus, the initial thermolysis product is regarded as a resonance hybrid of which (VIII) and (IX) are the main canonical forms. The



(VII)



(VIII)



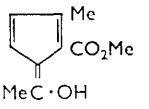
(IX)

mass spectral results are presented in a separate section at the end of the Discussion. Although *C*-acyl derivatives of α-amino- and α-hydroxyfulvenes have recently been investigated in detail, by Hafner [5] and others,[6] derivatives containing ester substituents have not been prepared previously. The properties of the *C*-acyl-α-amino- and *C*-acyl-α-hydroxyfulvenes are similar to the corresponding compounds in the present series, *i.e.*, nucleophilic substitutions of the α-substituents occur readily, the molecules contain strongly hydrogen-bonded 2-acyl groups, and tend to exist in the dipolar form.

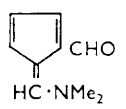
The location of the additional methoxycarbonyl and *C*-methyl groups of (VIII) follows from the interpretation of n.m.r. spectra and the general chemical properties. The n.m.r. spectrum of the acid hydrolysis product (X), *i.e.*, lacking the non-bonded ester group, showed the presence of two coupled nuclear protons ($J$ = 5 c./sec.) This coupling constant suggested, not only that these two protons were on adjacent carbons, but also that they were located at C-4 and C-5 rather than at C-3 and C-4. α,α-Dimethyl-, α,α-diphenyl-, and α,α-dibenzylfulvenes have been reported [7] with $J_{4,5}$ = *ca.* 5 c./sec., but $J_{3,4}$ = only *ca.* 2 c./sec. Furthermore, we have repeated the preparation of the fulvene (XI) [5] and obtained the values $J_{4,5}$ = 4·4, $J_{3,4}$ = 3·3, and $J_{3,5}$ = 1·4 c./sec. We have also synthesised (XII) (see below) and find $J_{4,5}$ = 4·8; $J_{2,4}$ and $J_{2,5}$ = 2·0 and 2·6 c./sec. Thus, by analogy, the acid hydrolysis product is formulated as (X).

[5] K. Hafner, C. Konig, M. Kreuder, G. Ploss, G. Schulz, E. Sturm, and K. H. Vopel, *Angew. Chem., Internat. Edn.*, 1963, **2**, 123; K. Hafner, K. H. Vopel, G. Ploss, and C. Konig, *Annalen*, 1963, **661**, 52; K. Hafner, G. Schulz, and K. Wagner, *ibid.*, 1964, **678**, 39; K. Hafner, H. E. A. Kramer, H. Musso, G. Ploss, and G. Schulz, *Chem. Ber.*, 1964, **97**, 2066.

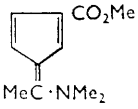
The fulvene (XII) was obtained by reaction of methyl cyclopentadienecarboxylate [8] with *NN*-dimethylacetamide diethyl acetal,[9] and the position of the ester group is assigned because of the lack of strong intramolecular hydrogen bonding (i.r. spectrum) in the corresponding amino-derivative. Although the starting product is normally represented as methyl cyclopenta-1,3-diene-1-carboxylate,[8] it is known that prototropic shifts can occur during certain reactions, *e.g.*, dimerisation.



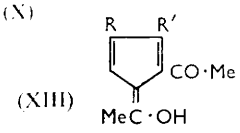
(X)



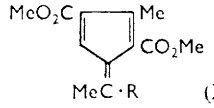
(XI)



(XII)



(XIII)



(XIV)

The second ester group in the thermolysis product (VIII) is not hydrogen bonded and it therefore occupies the C-4 position. Further evidence in support of this comes from the results of the acylation of the acid hydrolysis product (X). Under Friedel–Craft conditions this gave a *C*-acetyl derivative, the ultraviolet absorption of which closely resembled that of the alkaline hydrolysis product, *i.e.*, the *C*-acetyl group and the second ester grouping occupied the same relative position in the molecule. There is considerable experimental evidence to indicate that α-hydroxyfulvenes of type (X) will react preferentially at C-4 rather than at C-5. Thus when (X) was dissolved in 1,2-dimethoxyethane–deuterium oxide in the presence of a small amount of sodium deuteroxide, the exchange of hydrogen for deuterium occurred at the hydroxyl group and at C-4 rather than at C-5 as determined by the n.m.r. spectrum. It is also known from Hafner's work [5] that in the formylation of 2-formyl-α-hydroxyfulvenes, the second formyl group is introduced at C-4. Furthermore, we have acetylated 2-acetyl-α-hydroxy-α-methylfulvene [10] (XIII; R = R′ = H) and obtained (XIII; R = Ac; R′ = H), the position of entry of the second acetyl group being unambiguously shown by the n.m.r. spectrum, in that the two nuclear protons appeared as one singlet at τ 2·32. Hafner [5] has also recorded a similar observation with other 2,4-diacylfulvenes of this type.

Thus the thermolysis product of dimethyl 1,2,7-trimethylazepine-3,6-dicarboxylate (I) is the fulvene (XIV; R = NHMe) which yields (XIV; R = OH) after alkaline hydrolysis. It is evident that the formation of (XIV; R = NHMe) from (I) involves an extensive rearrangement, and it was this feature which led

[6] W. J. Linn and W. H. Sharkey, *J. Amer. Chem. Soc.*, 1957, **79**, 4970.

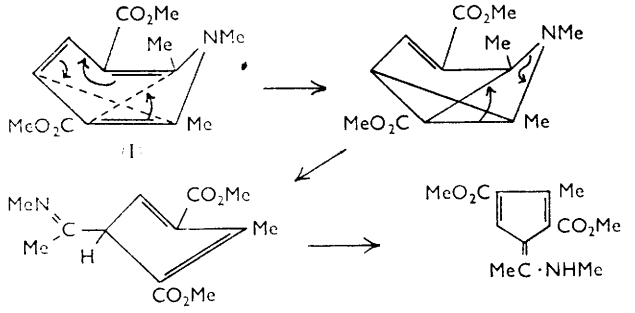
[7] W. B. Smith and B. A. Shoulders, *J. Amer. Chem. Soc.*, 1964, **86**, 3118.

[8] D. Peters, *J. Chem. Soc.*, 1959, 1761.

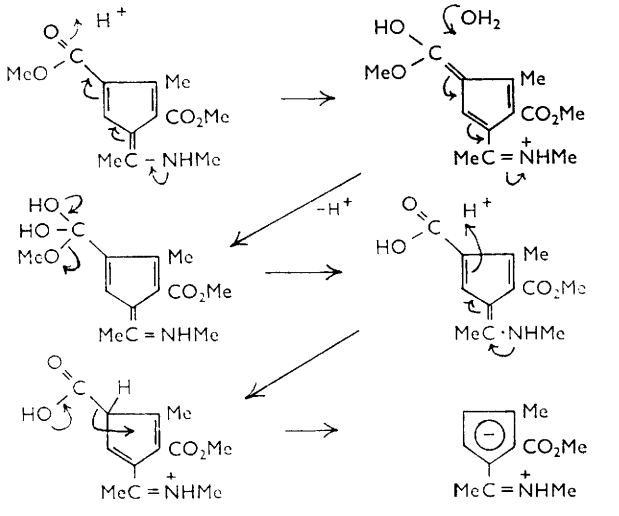
[9] H. Meerwein, W. Florian, N. Schön, and G. Stopp, *Annalen*, 1961, **641**, 1.

[10] K. Hafner, G. Schulz, and K. Wagner, *Annalen*, 1964, **678**, 39.

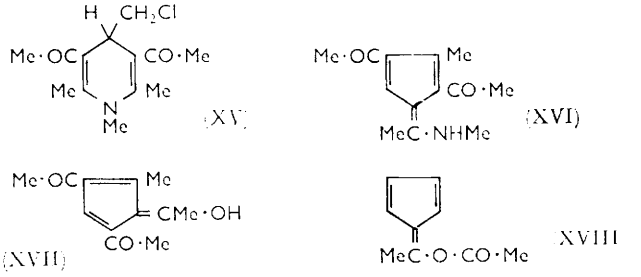
us initially to reject fulvene structures. The bicyclic derivative (VI) and the dihydropyridine (II; R = Me) presumably undergo an initial rearrangement to the 1*H*-azepine (I) prior to fulvene formation. A possible mechanism for the rearrangement of the *N*-methylazepine (I) to the fulvene (XIV; R = NHMe) is depicted below, it being assumed that the driving force is the resulting gain of aromatic stability.



The hydrolysis and decarboxylation of the 4-ester group of the thermolysis compound (XIV; R = NHMe), which accompanies the acid-catalysed substitution of the α-methylamino-group by hydroxyl is regarded as an initial hydrolysis of the non-bonded, sterically unhindered ester, aided by participation of the α-methylamino-grouping. This is followed by protonation of the ring and concerted decarboxylation. Participation of the α-methylamino-group is emphasised by the failure to bring about a similar hydrolysis and decarboxylation of the corresponding α-hydroxyfulvene (XIV; R = OH).



When dimethyl 4-chloromethyl-1,4-dihydro-2,6-dimethyl-1-phenylpyridine-3,5-dicarboxylate [1] (II; R = Ph) was heated it gave the fulvene (XIV; R = NHPh) although the yield was lower than with the *N*-methyl analogue. This fulvene was identical with the product obtained by the reaction of (XIV; R = OH) with aniline (see above). Thus, the rearrangement of 1,4-dihydropyridines of type (II) to *N*-substituted azepines of type (I), and the subsequent thermal rearrangement of these to fulvenes of type (XIV) seems to be a general reaction. As a further example, the dihydropyridine (XV) (cf. ref. 11) has been synthesised and when this was heated in mesitylene under reflux in the presence of barium carbonate, rearrangement to the fulvene (XVI) readily occurred. Base hydrolysis of (XVI) gave (XIII; R = Ac; R′ = Me). The position of the acidic proton in this compound has not been determined and other tautomeric structures, *e.g.*, (XVII) can be envisaged. The ultraviolet and infrared spectral properties of (XIII; R = Ac; R′ = H) were similar to those of (XIII; R = Ac; R′ = Me) and encouraged us to attempt an alternative synthesis of the latter derivative.



Hafner [10] obtained two products (XIII; R = R′ = H) and (XVIII) from the reaction of acetyl chloride with sodium cyclopentadienide. A repetition of this reaction using sodium methylcyclopentadienide gave a complex mixture from which two isomers (XIII; R = Me; R′ = H) and (XIII; R = H; R′ = Me) were obtained as crystalline solids. They were differentiated by their n.m.r. spectra as the former showed the two nuclear protons with identical chemical shifts and the latter showed the presence of the two adjacent nuclear protons with a coupling constant of 4 c./sec. Treatment of the isomer (XIII; R = Me; R′ = H) with acetyl chloride in the presence of stannic chloride caused no *C*-acetylation but a similar reaction with (XIII; R = H; R′ = Me) gave (XIII; R = Ac; R′ = Me), identical with the product obtained from (XV) by rearrangement and subsequent alkaline hydrolysis.

The very low values observed for the chemical shifts of the α-hydroxyl protons in the fulvenes containing 1,3-diacyl groups [*e.g.*, (XIII; R = Ac, R′ = H or Me)] or 1,3-diester groups (XIV; R = OH) is noteworthy. Thus in (XIII; R = Ac; R′ = H or Me) the values observed were τ −8·87 and −8·58, respectively, and the corresponding value for methyl 4-acetyl-α-hydroxy-3,α-dimethylfulvene-2-carboxylate was τ −6·39. The nature of the hydrogen bonding in 2-formyl-α-hydroxyfulvenes and its bearing on the low chemical shifts associated with the α-hydroxy-proton has been discussed [12] although the chemical shift values recorded were not so low as those now described.

*Mass Spectral Determinations.*—The mass spectra of

[11] E. Benary, *Ber.*, 1918, **51**, 577.
[12] K. Hafner, H. E. A. Kramer, H. Musso, G. Ploss, and G. Schulz, *Chem. Ber.*, 1964, **97**, 2066.

nine α-amino- (XIX)—(XXIV) and α-hydroxy-fulvenes (XXV)—(XXVII) have been determined and are reported in the Table and Figures 1—3. The fragmentation patterns of these compounds have been elucidated using deuterium labelling (crystallisation of α-deuterioxyfulvenes from methanol did not affect the percentage incorporation of deuterium) and high resolution measurements, and provide clear evidence of the relative location of substituents due to the operation of specific fragmentation processes.

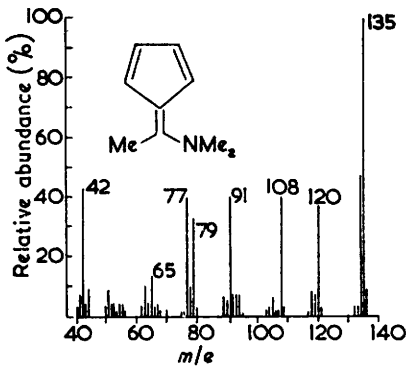



FIGURE 1

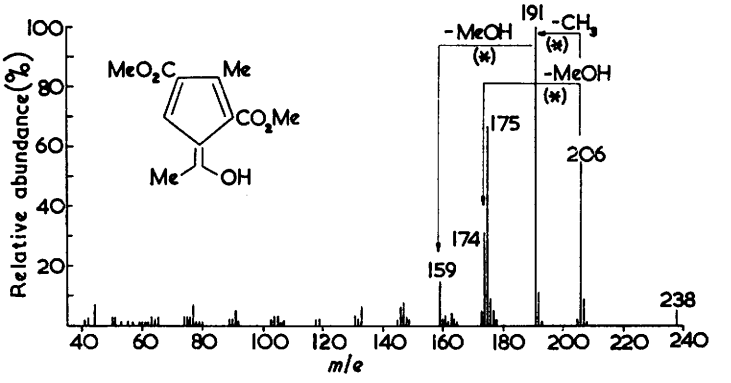



FIGURE 2

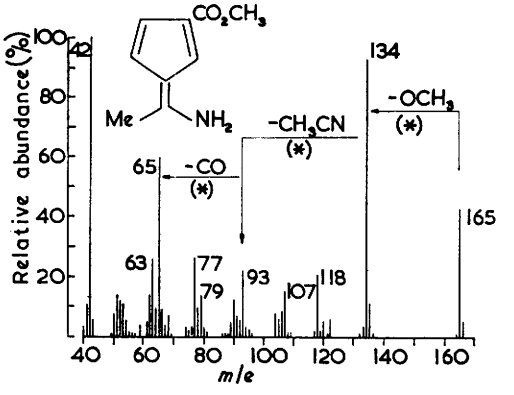
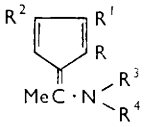
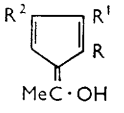



FIGURE 3

Mass spectra of fulvenes




(XIX; R = R¹ = R² = H, R³ = R⁴ = Me)
(XX; R = R² = R³ = R⁴ = H, R¹ = $CO_2$Me)
(XXI; R = R² = $CO_2$Me, R¹ = Me, R³ = R⁴ = H)
(XXII; R = R² = $CO_2$Me, R¹ = R³ = Me, R⁴ = H)
(XXIII; R = R² = H, R¹ = $CO_2$Me, R³ = R⁴ = H)
(XXIV; R = R² = $CO_2$Me, R¹ = R³ = R⁴ = Me)

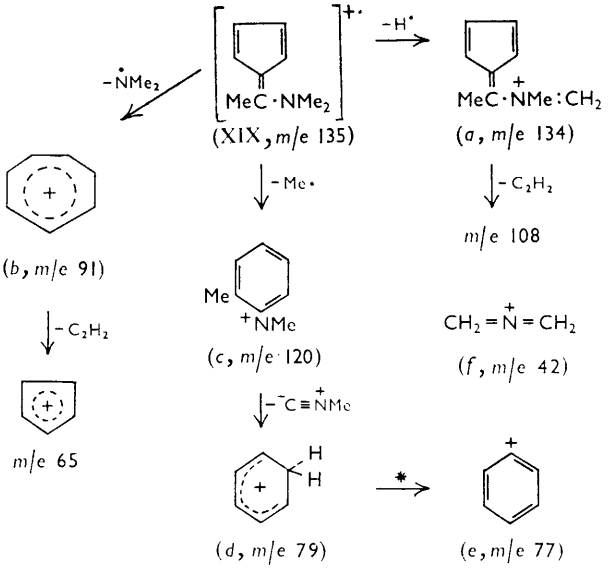



(XXV; R = $CO_2$Me, R¹ = Me, R² = H)
(XXVI; R = R² = $CO_2$Me, R¹ = Me)
(XXVII; R = $CO_2$Me, R¹ = Me, R² = COMe)

The unsubstituted α-dimethylaminofulvene (XIX) (Figure 1) shows the expected $M - 1$ ion (*a*, *m/e* 134) followed by loss of acetylene (*a* ⟶ *m/e* 108). The composition of the ion *m/e* 108 was established by the high-resolution measurement as $C_7H_{10}N$, thus ruling out the alternative path of loss of hydrogen cyanide from the molecular ion. Two further fragmentation paths operate with the generation of the tropylium ion (*b*, *m/e* 91) by loss of the dimethylamino-radical from the parent ion or loss of the elements of methyl cyanide from the $M$ — Me species (*c*, *m/e* 120) to give the benzenonium ion (*d*, *m/e* 79) which further decomposes by loss of a hydrogen molecule to the phenyl ion (*e*, *m/e* 77). All the α-dimethylaminofulvenes showed an ion at *m/e* 42 which is formulated as (*f*).

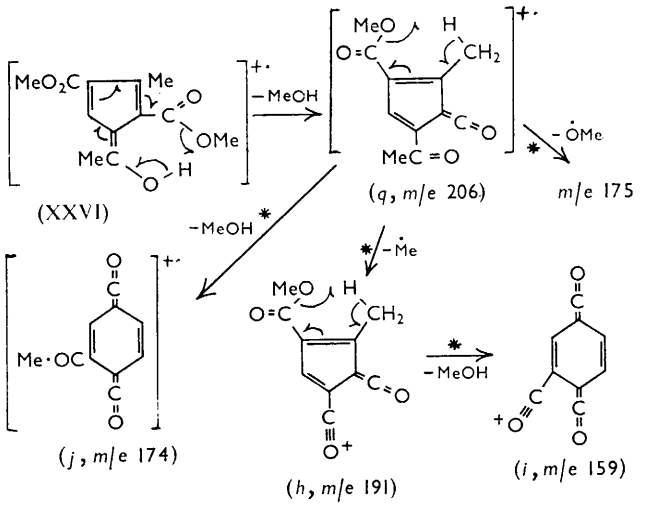
The introduction of ester substituents into the 2- and 4-positions modifies the breakdown pattern significantly. The fragmentation patterns of 2,4-dimethoxycarbonylfulvenes containing α-amino- (XXI), α-methylamino- (XXII), or α-hydroxyl- (XXVI) (Figure 2) substituents are similar, but differ markedly from that of α-amino-3-methoxycarbonyl-6-methylfulvene (XX) (Figure 3). The 2,4-dimethoxycarbonylfulvenes (XXI), (XXII), and (XXVI) exhibit large (55—96%) $M$ — MeOH ions, but the 3-methoxycarbonylfulvene (XX) has a negligible (4%) $M$ — MeOH ion. The involvement of the 2-methoxycarbonyl group is demonstrated by the fragmentation

of the 2-methoxycarbonylfulvene (XXV) which has an abundant (49%) $M$ — MeOH ion. The strong hydrogen bonding and high acidity exhibited by protons attached

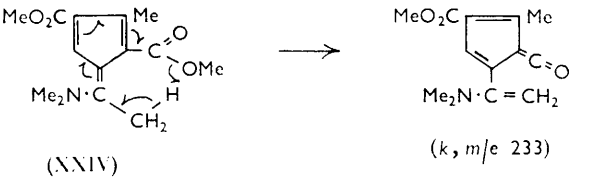



* Transitions supported by an appropriate metastable peak

to the hetero-atoms at C-α in 2-methoxycarbonylfulvenes suggested that these were involved in the fission of methanol and this was demonstrated by deuterium-labelling experiments. Thus methanol is lost *via* a 7-membered cyclic transition state (XXVI ⟶ *g*).



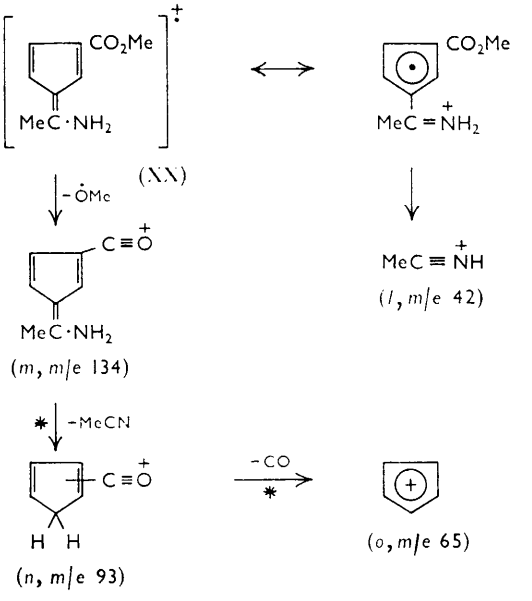

Related processes have been observed with *o*-methoxybenzoic acid and *o*-ethoxybenzamide which exhibit $M - H_2O$ [13] and $M - NH_3$ [14] ions, respectively. The ease of loss of methanol from (XXVI) is related to the acidity of the proton attached to the hetero-atom at C-α and is demonstrated by the relatively small abundance (10%) of the $M$ — MeOH ion in the α-dimethylaminofulvene (XXIV), in which an analogous cyclic process involving the α-methyl substituent can operate (XXIV ⟶ *k*).




A study of molecular models of (XXI), (XXII), (XXIV), and (XXVI) indicates that the hydrogen involved in this process can approach the ether oxygen of the ester to within 1 Å, which is well within the limiting interatomic distance of 1·8 Å for a hydrogen-transfer reaction induced by electron-impact.[15]

Further fragmentation of the $M$ — MeOH species (*g*, *m/e* **206**) proceeds by loss of a methyl radical to give (*h*, *m/e* **191**) followed by loss of methanol generating (*i*, *m/e* **159**). The other structurally important fragmentation involves loss of methanol to give (*j*, *m/e* **174**). The *ortho*-effects operative between C-3 and C-4 (*h* ⟶ *i* and *g* ⟶ *j*) provide further structural information.

In contrast to the behaviour of (XXVI) the base peak in the spectrum of α-amino-3-methoxycarbonyl-α-methylfulvene (XX) arises by fission of the C-1–C-α bond with concomitant hydrogen rearrangement (XX ⟶ *l*).




Metastable ions provide support for the fragmentation path *m* ⟶ *n* ⟶ *o* and also for the conversion of the benzenonium ion (*m/e* **79**) to the phenyl ion (*m/e* **77**).

[13] T. Aczel and H. E. Lumpkin, *Anal. Chem.*, 1961, **33**, 386.
[14] G. Spiteller, *Monatsh.*, 1961, **92**, 1147.
[15] C. Djerassi and L. Tökés, *J. Amer. Chem. Soc.*, 1966, **88**, 536.

Mass spectra of fulvenes *

| Compound | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (XIX) | *m/e* | 32 | 39 | 41 | 42 | 44 | 51 | 63 | 65 | 77 | 78 | 79 | 89 | 90 | 91 | 92 | 93 | 94 | 105 | 108 | 118 |
| | (I) (%) | 5 | 15 | 7 | 43 | 9 | 9 | 10 | 13 | 40 | 10 | 33 | 6 | 5 | 40 | 7 | 7 | 7 | 6 | 40 | 8 |
| | *m/e* | 119 | 120 | 134 | 135 | 136 | | | | | | | | | | | | | | | |
| | (I) (%) | 7 | 37 | 47 | 100 | 9 | | | | | | | | | | | | | | | |
| (XX) | *m/e* | 38 | 39 | 41 | 92 | 43 | 50 | 51 | 52 | 53 | 54 | 61 | 62 | 63 | 64 | 65 | 66 | 68 | 77 | 78 | 79 |
| | (I) (%) | 7 | 18 | 11 | 100 | 5 | 7 | 14 | 12 | 11 | 5 | 5 | 14 | 26 | 9 | 10 | 9 | 7 | 27 | 10 | 14 |
| | *m/e* | 89 | 90 | 91 | 92 | 93 | 104 | 105 | 106 | 118 | 120 | 122 | 134 | 135 | 165 | 166 | metastables at 109, 64·5, | | | | |
| | (I) (%) | 5 | 12 | 7 | 5 | 22 | 8 | 6 | 9 | 21 | 6 | 6 | 93 | 11 | 43 | 6 | 45·5, and 75·2 | | | | |
| (XXVI) | *m/e* | 31 | 32 | 44 | 77 | 91 | 133 | 146 | 147 | 173 | 174 | 175 | 176 | 177 | 191 | 192 | 206 | 207 | 238 | | |
| | (I) (%) | 13 | 8 | 7 | 7 | 5 | 5 | 6 | 8 | 5 | 31 | 67 | 9 | 5 | 100 | 11 | 55 | 9 | 5 | | |
| | metastables at 147, 132·5, and 177·2 | | | | | | | | | | | | | | | | | | | | |
| (XXI) | *m/e* | 41 | 42 | 44 | 51 | 77 | 91 | 103 | 118 | 119 | 145 | 146 | 147 | 158 | 162 | 173 | 174 | 175 | 177 | 190 | 204 |
| | (I) (%) | 5 | 10 | 27 | 6 | 8 | 7 | 5 | 5 | 5 | 16 | 22 | 7 | 5 | 5 | 47 | 100 | 15 | 5 | 25 | 9 |
| | *m/e* | 205 | 206 | 207 | 237 | 238 | | | | | | | | | | | | | | | |
| | (I) (%) | 78 | 31 | 5 | 67 | 8 | | | | | | | | | | | | | | | |
| (XXII) | *m/e* | 44 | 50 | 51 | 55 | 56 | 63 | 65 | 75 | 76 | 77 | 89 | 90 | 91 | 94 | 102 | 103 | 104 | 105 | 116 | 117 |
| | (I) (%) | 7 | 7 | 11 | 9 | 38 | 7 | 8 | 7 | 6 | 13 | 6 | 6 | 10 | 6 | 5 | 9 | 6 | 6 | 6 | 8 |
| | *m/e* | 118 | 119 | 130 | 131 | 132 | 133 | 147 | 158 | 159 | 160 | 161 | 162 | 174 | 176 | 187 | 188 | 189 | 204 | 205 | 218 |
| | (I) (%) | 5 | 11 | 13 | 13 | 8 | 8 | 6 | 8 | 29 | 28 | 9 | 9 | 9 | 5 | 30 | 100 | 18 | 37 | 6 | 8 |
| | *m/e* | 219 | 220 | 251 | 252 | | | | | | | | | | | | | | | | |
| | (I) (%) | 97 | 23 | 22 | 4 | | | | | | | | | | | | | | | | |
| (XXIII) | *m/e* | 42 | 43 | 44 | 56 | 77 | 89 | 91 | 94 | 108 | 117 | 118 | 119 | 132 | 133 | 134 | 135 | 162 | 163 | 178 | 192 |
| | (I) (%) | 12 | 40 | 10 | 20 | 7 | 5 | 10 | 7 | 14 | 7 | 13 | 7 | 20 | 11 | 30 | 6 | 70 | 10 | 18 | 13 |
| | *m/e* | 193 | 194 | | | | | | | | | | | | | | | | | | |
| | (I) % | 100 | 12 | | | | | | | | | | | | | | | | | | |
| (XXIV) | *m/e* | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 63 | 64 | 65 |
| | (I) (%) | 8 | 13 | 60 | 420 | 90 | 17 | 19 | 9 | 25 | 9 | 7 | 5 | 10 | 85 | 9 | 115 | 13 | 12 | 6 | 15 |
| | *m/e* | 66 | 70 | 72 | 73 | 75 | 76 | 77 | 78 | 79 | 89 | 90 | 91 | 94 | 101 | 102 | 103 | 104 | 105 | 108 | 115 |
| | (I) (%) | 6 | 5 | 9 | 5 | 9 | 8 | 35 | 13 | 11 | 10 | 7 | 18 | 5 | 14 | 9 | 19 | 11 | 11 | 5 | 6 |
| | *m/e* | 116 | 117 | 118 | 119 | 129 | 130 | 131 | 132 | 133 | 142 | 144 | 145 | 146 | 147 | 148 | 157 | 158 | 159 | 160 | 162 |
| | (I) (%) | 5 | 13 | 7 | 9 | 5 | 10 | 22 | 18 | 8 | 4 | 7 | 8 | 100 | 18 | 11 | 16 | 6 | 14 | 5 | 7 |
| | *m/e* | 169 | 172 | 173 | 174 | 175 | 176 | 178 | 188 | 189 | 190 | 191 | 202 | 204 | 205 | 206 | 207 | 218 | 220 | 232 | 233 |
| | (I) (%) | 8 | 5 | 10 | 33 | 12 | 5 | 5 | 6 | 7 | 11 | 5 | 20 | 7 | 7 | 30 | 10 | 16 | 7 | 10 | 10 |
| | *m/e* | 234 | 235 | 250 | 264 | 265 | 266 | | | | | | | | | | | | | | |
| | (I) (%) | 35 | 6 | 10 | 7 | 60 | 9 | | | | | | | | | | | | | | |
| (XXV) | *m/e* | 43 | 45 | 51 | 77 | 78 | 79 | 91 | 105 | 106 | 122 | 133 | 134 | 137 | 138 | 148 | 149 | 165 | 180 | | |
| | (I) (%) | 21 | 5 | 12 | 21 | 5 | 6 | 5 | 22 | 6 | 6 | 100 | 10 | 4 | 6 | 49 | 9 | 3 | 11 | | |
| (XXVII) | *m/e* | 43 | 44 | 77 | 91 | 119 | 133 | 147 | 175 | 176 | 190 | 191 | 222 | 223 | | | | | | | |
| | (I) (%) | 22 | 5 | 5 | 5 | 5 | 6 | 6 | 100 | 18 | 60 | 11 | 37 | 5 | | | | | | | |

* All ions having an abundance of 5% or more of the base peak (100%) are recorded in the Table; in addition ions of lesser abundance are included if they are of diagnostic value.

## EXPERIMENTAL

Ultraviolet spectra were determined on ethanolic solutions with a Unicam S.P. 700 instrument and infrared spectra (only main maxima quoted) were measured for carbon tetrachloride solutions (except where otherwise stated) with a Unicam S.P. 100 instrument (corrected values given). N.m.r. spectra were measured for carbon tetrachloride solutions on a Perkin-Elmer R.10 spectrometer operating at 60 Mc./sec. M. p.'s are uncorrected (Kofler hot-stage apparatus) and molecular weights were determined with a Mecrolab vapour pressure osmometer, model 301A. All mass spectra were obtained by direct insertion of the sample into the ion source of an A.E.I. MS9 mass spectrometer. The energy of the electron beam was 70 e.v. Light petroleum refers to the fraction, b. p. 40—60°.

*Dimethyl 3,α-Dimethyl-α-methylaminofulvene-2,4-dicarboxylate* (XIV; R = NHMe).—(*a*) Dimethyl 4-chloromethyl-1,4-dihydro-1,2,6-trimethylpyridine-3,5-dicarboxylate (I; R = Me) (50 g.) was ground with barium carbonate (50 g.) and stirred rapidly into refluxing mesitylene (250 ml.) until all the dihydropyridine had undergone reaction (4—6 hr.). The solvent was removed *in vacuo*, and the residue treated with cold dilute aqueous hydrochloric acid. The organic material was separated, washed with water and ethanol, and then dried. Chromatography on silica with carbon tetrachloride–chloroform (3 : 1) as the eluent followed by crystallisation from ethanol gave a colourless crystalline *solid* (22 g., 50%), m. p. 175—177° (Found: C, 61·7; H, 6·8; N, 6·0; OMe, 29·95%; *M*, 244. $C_{13}H_{17}NO_4$ requires C, 62·15; H, 6·8; N, 5·6; OMe, 24·7%; *M*, 251), $\lambda_{max.}$ 202, 232, 272, and 364 mμ (ε 7690, 6910, 33,600, and 22,000, respectively); $\nu_{max.}$ 1710, 1640, and 1617 cm.$^{-1}$. The n.m.r. spectrum ($CDCl_3$) showed resonances at τ −3·0 (broad s; iminium proton), 2·42 (s; nuclear proton), 6·15 and 6·20 (both s; *O*-methyls), 6·84 (d; $J$ = 5·5 c./sec.; iminium *N*-methyl group), 7·28 and 7·55 (*C*-methyls).

The fulvene (25 mg.) was dissolved in dry 1,2-dimethoxyethane (0·5 ml.) and deuterium oxide (0·1 ml.) and kept for 4 days at 30°. The solvent was removed *in vacuo*, and the n.m.r. spectrum ($CDCl_3$) of the residue showed the iminium proton had been replaced. The mass spectrum of the product indicated 28% monodeuteration and 8% dideuteration (calculated according to Djerassi [16]).

(*b*) The same product was obtained in quantitative yield

[16] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structural Elucidation of Natural Products by Mass Spectrometry, Vol. I, Alkaloids," Holden Day, San Francisco, 1964, p. 34.

from dimethyl 1,2,7-trimethylazepine-3,6-dicarboxylate (I) by sublimation through a preheated tube containing 2 in. of fine sand at 130°/0·1 mm. Sublimation at 80°/1 mm. gave the unchanged azepine ester.

(*c*) The foregoing azepine ester (15 mg.) in dry benzene (15 ml.) was heated under reflux for 20 hr. Removal of the solvent gave the above pyrolysis product in quantitative yield.

(*d*) Dimethyl α-hydroxy-3,α-dimethylfulvene-2,4-dicarboxylate (see below) (XIV; R = OH) (100 mg.) was treated with a saturated methanolic solution (50 ml.) of anhydrous methylamine at 100° for 6 hr. in a Carius tube. Removal of the solvent from the product followed by chromatography on alumina with carbon tetrachloride–chloroform (3 : 1) as the eluent gave the product (84 mg., 80%), m. p. 175—177°, identical in all respects with the original thermolysis product.

*Dimethyl α-Hydroxy-3,α-dimethylfulvene-2,4-dicarboxylate.*—The above thermolysis product (1·5 g.) was suspended in an aqueous solution (25 ml.) of potassium hydroxide (0·6 g.) and heated under reflux for 30 min. Residual starting material was removed by extraction of the solution with ether. Acidification with hydrochloric acid gave a solid which was separated, dried, crystallised from ethanol, and finally sublimed at 80—90°/0·1 mm. The *product* formed pale yellow hexagonal prisms (1·21 g., 86%), m. p. 100—102° (Found: C, 60·6; H, 6·1; OMe, 27·4%; *M*, 226. $C_{12}H_{14}O_5$ requires C, 60·5; H, 5·9; OMe, 26·1%; *M*, 238), $\lambda_{max.}$ 256 and 334 mμ (ε 29,700 and 14,400); $\lambda_{infl.}$ 231 mμ (ε 10,100); $\nu_{max.}$ 1724 and 1609 cm.$^{-1}$. The n.m.r. spectrum showed resonances at τ −6·48 (s; $=\overset{+}{O}H$), 2·23 (s; nuclear proton), 6·03, 6·16 (both s; *O*-methyls), 7·30 and 7·46 (both s; *C*-methyls).

The fulvene (25 mg.) was dissolved in dry 1,2-dimethoxyethane (0·5 ml.) and deuterium oxide (0·2 ml.) and a trace of sodium was added. The mixture was kept at 30° for 3 days after which the solvent was removed *in vacuo*. The residue was extracted into ether to give, after removal of the solvent, a green solid, m. p. 55—60°. This was divided into two portions. The first was sublimed at 90°/0·1 mm. to give a yellow solid, and the second crystallised from methanol. The mass spectra of both products were identical and indicated [16] 40% monodeuteration and 20% dideuteration.

*Dimethyl α-Amino-3,α-dimethylfulvene-2,4-dicarboxylate* (XIV; R = $NH_2$).—The hydrolysis product (XIV; R = OH) (0·5 g.; containing $=\overset{+}{O}H$) was heated for 5·5 hr. with an anhydrous saturated methanolic solution of ammonia. After removal of the solvent, the oily solid was chromatographed on silica using carbon tetrachloride–chloroform (3 : 1) for elution and the main *product* was sublimed at 160°/0·1 mm. to give a pale buff crystalline solid (0·42 g., 84%), m. p. 177—178° (Found: C, 60·8; H, 6·2; N, 5·7%; *M*, 234. $C_{12}H_{15}NO_4$ requires C, 60·75; H, 6·35; N, 5·9%; *M*, 237), $\lambda_{max.}$ 270 and 358 mμ (ε 35,000 and 22,200); $\nu_{max.}$ 3464, 3335, 1698, 1685, 1656, and 1623 cm.$^{-1}$. The n.m.r. spectrum contained singlets at τ −2·0 (bonded NH), 2·57 (nuclear proton), 3·4 (non-bonded NH), 6·30 and 6·35 (*O*-methyls), 7·45 and 7·60 (*C*-methyls). The NH bands were broad.

*Dimethyl 3,α-Dimethyl-α-dimethylaminofulvene-2,4-dicarboxylate* (XIV; R = $NMe_2$).—The hydrolysis product (180 mg., containing $=\overset{+}{O}H$) was heated with a saturated solution of anhydrous dimethylamine in methanol (30 ml.) in a Carius tube for 4 hr. at 100°. Chromatography of the product on silica as before gave a yellow crystalline solid (20 mg., 10%), m. p. 167—168° (Found: C, 63·0; H, 6·9; N, 5·15. $C_{14}H_{19}NO_4$ requires C, 63·4; H, 7·2; N, 5·3%), $\lambda_{max.}$ 242, 278, and 382 mμ (ε 11,800, 24,200, and 17,300, respectively); $\lambda_{infl.}$ 269 mμ (ε 21,500); $\nu_{max.}$ 1701, 1686, 1670, and 1584 cm.$^{-1}$. The n.m.r. spectrum ($CDCl_3$) contained singlets at τ 2·98 (nuclear proton), 6·27 (*O*-methyl), 6·62 (*N*-methyl), 7·39 and 7·50 (*C*-methyls).

*Dimethyl α-Anilino-3,α-dimethylfulvene-2,4-dicarboxylate* (XIV; R = NHPh).—(*a*) The hydrolysis product (100 mg., containing $=\overset{+}{O}H$) was dissolved in anhydrous methanol (10 ml.) containing aniline (100 mg.) and was heated at 100° for 18 hr. in a Carius tube. The resulting product was cooled to 0°, and the *α-anilinofulvene* separated and washed with a little cold methanol. Crystallisation from methanol–chloroform gave the fulvene as yellow needles (114 mg., 88%), m. p. 216—220° (decomp.) (Found: C, 69·2; H, 6·35; N, 4·6. $C_{18}H_{19}NO_4$ requires C, 69·0; H, 6·1; N, 4·5%), $\lambda_{max.}$ 272 and 382 mμ (ε 35,700 and 27,600); $\nu_{max.}$ (KBr) 1594, 1609, 1623, and 1697 cm.$^{-1}$. The n.m.r. spectrum ($CDCl_3$) showed peaks at τ −4·76 (broad, imino-proton), 2·20 (s; nuclear proton), 2·52 (multiplet, phenyl protons), 6·06, 6·14 (s; *O*-methyls), 7·20 and 7·44 (*C*-methyls).

(*b*) Dimethyl 4-chloromethyl-1,4-dihydro-2,6-dimethyl-1-phenylpyridine-3,5-dicarboxylate [1] was mixed with barium carbonate and heated at 160°/0·1 mm. The sublimate was combined with a chloroform extract of the non-volatile residue and the solution chromatographed on deactivated alumina (10% water), with chloroform–carbon tetrachloride (1 : 1) as the eluent. Addition of alcohol to the second fraction gave the fulvene as a buff-coloured solid which was purified further by crystallisation from methanol–chloroform (*ca.* 10% yield), when it formed yellow needles, m. p. 215—220° (decomp.), alone or mixed with the product from the previous experiment. The infrared spectrum was also identical with that of the previous product.

*Dimethyl α-p-Chloranilino-3,α-dimethylfulvene-2,4-dicarboxylate* (XIV; R = *p*-$C_6H_4Cl$).—The hydrolysis product (0·35 g., containing $=\overset{+}{O}H$) was heated with *p*-chloraniline (0·5 g.) in anhydrous methanol (50 ml.) in a Carius tube at 100° for 18 hr. The solid obtained after cooling the reaction product, was crystallised from methanol to give yellow crystals (0·5 g., 98%), m. p. 159·5—160·5° (Found: C, 62·2; H, 5·0; N, 3·9. $C_{19}H_{18}ClNO_4$ requires C, 62·15; H, 5·2; N, 4·05%), $\lambda_{max.}$ 270 and 386 mμ (ε 37,000 and 30,900); $\nu_{max.}$ 1697, 1613, and 1595 cm.$^{-1}$. The n.m.r. spectrum contained resonances at τ −4·7 (broad s; NH), 2·70 (q; $J$ = 9 c./sec.; a simplified $A_2B_2$ system), 6·10 and 6·18 (both s; *O*-methyls), 7·24 and 7·46 (both s; *C*-methyls).

*Methyl α-Hydroxy-3,α-dimethylfulvene-2-carboxylate* (X).—The thermolysis product (0·5 g.) was suspended in 0·5N-sulphuric acid (50 ml.) and distilled in steam. The yellow solid which separated from the distillate was removed by filtration, washed, and dried. Chromatography on silica using ether–light petroleum (1 : 9) for elution followed by sublimation at 65°/0·1 mm. gave the *product* as yellow crystals (0·27 g., 71·5%), m. p. 70—71° (Found: C, 66·8; H, 6·75%; *M*, 171. $C_{10}H_{12}O_3$ requires C, 66·65; H, 6·7%; *M*, 180), $\lambda_{max.}$ 231, 325, and 355 mμ (ε 14,950, 15,200, and 7580, respectively); $\nu_{max.}$ 1620 cm.$^{-1}$. The n.m.r. spectrum showed resonances at τ −5·53 (s; $=\overset{+}{O}H$; slowly exchanged

in $D_2O$, see below), 3·14 (C-5 proton), and 3·94 (C-4 proton) (both d; $J = 5$ c./sec.; adjacent ethylenic protons), 6·11 (s; *O*-methyl), 7·6 and 7·62 (*C*-methyls).

The fulvene (3 mg.) was dissolved in chloroform (0·5 ml.) and deuterium oxide (0·1 ml.) was added. The mixture was shaken periodically over 18 hr. and the solvent then removed *in vacuo*. The mass spectrum of the product showed that 64% monodeuteration had occurred. In another experiment, the fulvene (30 mg.) was dissolved in dry 1,2-dimethoxyethane (0·4 ml.) and deuterium oxide (0·15 ml.) with a trace of sodium (*ca.* 0·5 mg.) present. After 18 hr. at 20°, the solvent was removed *in vacuo*, and the residue extracted with ether. The n.m.r. spectrum of the solid obtained after removal of the ether contained a broadened singlet at *ca.* $\tau$ 3·1, but the signal at $\tau$ 3·94 had largely disappeared. After crystallisation from methanol, the product was subjected to mass spectral analysis which indicated that 41% monodeuteration, 26% dideuteration, and 9% trideuteration had occurred.

*Methyl α-Amino-3,α-dimethylfulvene-2-carboxylate*.—The foregoing product (100 mg.) was heated in a Carius tube with saturated anhydrous methanolic ammonia (30 ml.) at 100° for 4 hr. After removal of the solvent, the product was chromatographed on silica with ether–light petroleum (1 : 1) as the eluent to yield the *product* as a yellow crystalline solid (50 mg., 50%), m. p. 107—108° (Found: C, 66·8; H, 7·3; N, 7·75. $C_{10}H_{13}NO_2$ requires C, 67·0; H, 7·3; N, 7·8%), $\lambda_{max.}$ 239 and 363 mμ (ε 18,100 and 16,100); $\lambda_{infl.}$ 346 mμ (ε 14,600); $\nu_{max.}$ 1628 cm.$^{-1}$. The n.m.r. spectrum showed resonances at $\tau$ −2·5 and 4·6 (iminium protons), 3·34 and 4·12 (both d; $J = 5$ c./sec.; adjacent ethylenic protons), 6·24 (s; *O*-methyl), 7·70 (s; *C*-methyls).

*Methyl 4-Acetyl-α-hydroxy-3,α-dimethylfulvene-2-carboxylate*.—Methyl α-hydroxy-3,α-dimethylfulvene-2-carboxylate (X; above; 130 mg.) was dissolved in dry carbon disulphide (40 ml.) and treated with acetyl chloride (0·4 ml.) and anhydrous stannic chloride (0·44 g.). The mixture was heated under reflux for 2 hr. before pouring into water (20 ml.). The aqueous layer was separated and washed with chloroform (10 ml.) and the combined organic extracts dried ($MgSO_4$). Removal of the solvent gave a solid which was purified by two sublimations at 85°/0·1 mm. to give yellow needles (30 mg., 19%), m. p. 104—105° (Found: C, 64·6; H, 6·55. $C_{12}H_{14}O_4$ requires C, 64·85; H, 6·35%), $\lambda_{max.}$ 229, 270, and 349 mμ (ε 6340, 29,100 and 13,050, respectively); $\nu_{max.}$ 1609, 1674 (ε 385) cm.$^{-1}$. The n.m.r. spectrum showed peaks at $\tau$ −6·39 (s; hydroxyl proton), 2·68 (s; nuclear proton), 6·05 (s; *O*-methyl), 7·41, 7·50, and 7·66 (all s; *C*-methyls).

*Methyl α-Dimethylamino-α-methylfulvene-3-carboxylate* (XII).—Methyl cyclopentadienecarboxylate (5 g., obtained by distillation of the dimer [8]) was dissolved in ethanol (10 ml.) at −60°, and a solution of *NN*-dimethylacetamide diethyl acetal [9] (3 g.) in the minimum amount of ether was added. The mixture was allowed to warm slowly to room temperature and then kept for 20 hr. Removal of the solvents gave an oily residue which was chromatographed on silica, the product being eluted with ether–chloroform (4 : 1). Crystallisation from cyclohexane gave a buff-coloured solid (100 mg.), m. p. 113—115° (Found: C, 68·2; H, 7·8; N, 7·5. $C_{11}H_{15}NO_2$ requires C, 68·35; H, 7·8; N, 7·25%), $\lambda_{max.}$ 254 and 353 mμ (ε 13,700 and 31,500); $\nu_{max.}$ 1713, 1589 cm.$^{-1}$. The n.m.r. spectrum ($CDCl_3$) showed signals at 7·59 (s; *N*-methyls), 7·50 (s; *C*-methyl), 6·21 (s; *O*-methyl), an ABX system from the nuclear protons with $\nu_A$ $\tau$ 3·26, $\nu_B$ 3·48, and $\nu_X$ $\tau$ 2·75 ($J_{AX} = 2·03$, $J_{AB} = 4·75$, and $J_{BX} = 2·57$ c./sec.).

*Methyl α-Amino-α-methylfulvene-3-carboxylate*.—The above dimethylamino-derivative (25 mg.) was heated with dry methanol (40 ml.) saturated with dry ammonia at 70° for 16 hr. The solvent was removed and the mixture purified by chromatography on silica, with ether–chloroform (65 : 35) as the eluent. The product was a yellow oil which rapidly crystallised to a yellow solid (13 mg., 60%), m. p. 179—183°, raised to 187—188·5° after sublimation at 170°/0·1 mm. [Found: *M* (mass spectroscopy), 165. $C_9H_{11}NO_2$ requires *M*, 165]; $\lambda_{max.}$ 253 and 345 mμ (ε 14,900 and 28,800); $\nu_{max.}$ ($CHCl_3$) 1692, 1651 (infl.), 1630, 1601 (infl.), and 1583 cm.$^{-1}$. The n.m.r. spectrum ($Me_2CO$) showed signals at $\tau$ 7·54 (s; *C*-methyl), 6·30 (s; *O*-methyl), 3·45 and 2·65 (multiplets from nuclear protons), and 2·25 (broad s; amino-protons).

*3,5-Diacetyl-4-chloromethyl-1,4-dihydro-1,2,6-trimethylpyridine* (XV).—Pentane-2,4-dione monomethylimine [17] (2 g.), 1,2-dichloroethyl ethyl ether [18] (1·5 ml.), and diethyl ether (4 ml.) were shaken until homogeneous and then kept in an open flask for 2 days. Water (15 ml.) was added and the *dihydropyridine* separated. Crystallisation from ethanol gave yellow prisms (0·4 g., 18%), m. p. 120—121° (Found: C, 60·8; H, 7·4; N, 5·6. $C_{13}H_{18}ClNO_2$ requires C, 61·1; H, 7·1; N, 5·5%), $\lambda_{max.}$ 255, 275, and 364 mμ; (ε 13,200, 8240, and 8280, respectively); $\nu_{max.}$ 1560, 1610, and 1661 cm.$^{-1}$. The n.m.r. spectrum ($CDCl_3$) showed resonances at $\tau$ 5·84 (t; nuclear proton), 6·72 (s; *N*-methyl), 6·84 (d; 4-chloromethyl), 7·65 and 7·67 (both s; *C*-methyls).

*2,4-Diacetyl-3,α-dimethyl-α-methylaminofulvene* (XVI).—The foregoing dihydropyridine (500 mg.) in refluxing mesitylene (50 ml.) was stirred vigorously with barium carbonate (1·5 g.) until the reaction was complete (5—10 min.; followed by ultraviolet spectral measurements). The solvent was removed under reduced pressure and the remaining solid extracted with chloroform (Soxhlet). Chromatography on alumina (deactivated with 10% water) with carbon tetrachloride–chloroform (3 : 2) as the eluent gave a buff-coloured solid, which, after crystallisation from ethanol, formed yellow needles (210 mg., 49%), m. p. 195—197° (Found: C, 71·4; H, 7·95; N, 6·65. $C_{13}H_{17}NO_2$ requires C, 71·2; H, 7·8; N, 6·4%), $\lambda_{max.}$ 249, 297, and 377 mμ (ε 6860, 40,000, and 11,500, respectively); $\nu_{max.}$ (KBr) 1572, 1638, and 1665 cm.$^{-1}$, and in $CHCl_3$, 1644 cm.$^{-1}$ (ε 546). The n.m.r. spectrum ($CDCl_3$) contained peaks at $\tau$ −4·6 (broad; imino-proton), 2·27 (s; nuclear proton), 6·76 (d; $J = 5$ c./sec., *N*-methyl), 7·21, 7·41, 7·44, and 7·52 (all s; *C*-methyls).

The same fulvene was obtained in lower yield (*ca.* 20%) by heating a mixture of the dihydropyridine and barium carbonate in a sublimation tube at 150°.

*2,4-Diacetyl-α-hydroxy-3,α-dimethylfulvene* (XIII; R = CO·Me, R′ = Me).—(*a*) The foregoing α-methylaminofulvene (200 mg.) was heated on the steam-bath with an aqueous solution (15 ml.) of potassium hydroxide (200 mg.). After cooling, the product was extracted with chloroform (2 × 10 ml.) to remove unchanged material and the aqueous layer was acidified with hydrochloric acid. The precipitate was extracted into ether (3 × 20 ml.), dried ($MgSO_4$), and chromatographed on silica after concentration. The

[17] E. Knoevenagel and W. Ruschhaupt, *Ber.*, 1898, **31**, 1025.
[18] A. W. Johnson, *J. Chem. Soc.*, 1946, 895.

product was eluted with ether and the first fraction, after removal of solvent, was sublimed at 120°/0·1 mm. to give yellow needles (100 mg., 53%), m. p. 124—125° (Found: C, 70·0; H, 6·7. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·85%) $\lambda_{max.}$ 282, 340, and 375 mμ (ε 37,900, 7000, and 8480, respectively); $\lambda_{infl.}$ 244 mμ (ε 6560) and in ethanolic sodium hydroxide, $\lambda_{max.}$ 248, 301, and 353 mμ; $\nu_{max.}$ 1568, 1617, and 1670 (ε 636) cm.$^{-1}$. The n.m.r. spectrum showed resonances at τ −8·87 (s; hydroxyl proton), 2·34 (s; nuclear proton), 7·25, 7·38, 7·42, and 7·60 (all s; *C*-methyls).

(*b*) 2-Acetyl-α-hydroxy-3,α-dimethylfulvene (10 mg.) (see below) in dry carbon disulphide (10 ml.) was treated with redistilled acetyl chloride (11 mg.) and anhydrous stannic chloride (22 mg.). The mixture was stirred at room temperature for 3 hr., poured into water (20 ml.), and the organic layer separated. The aqueous layer was extracted with chloroform (10 ml.) and the combined organic extracts dried ($MgSO_4$). The residue obtained after removal of the solvent *in vacuo* was chromatographed on silica and eluted with light petroleum–ether (1 : 4). The second fraction obtained was fractionally sublimed at 100°/0·1 mm. and gave yellow needles (1·6 mg., 13%), m. p. 124—125°, alone and when mixed with the previous specimen.

A similar reaction performed with 2-acetyl-α-hydroxy-4,α-dimethylfulvene (below) gave only unchanged starting material.

2,4-*Diacetyl-α-hydroxy-α-methylfulvene* (XIII; R = CO·Me, R′ = H).—2-Acetyl-α-hydroxy-α-methylfulvene [10] (400 mg.) in dry carbon disulphide (100 ml.) was stirred with freshly distilled acetyl chloride (0·44 g.) and stannic chloride (0·89 g.) at room temperature for 4 hr. The reaction mixture was poured into water (100 ml.) and the organic layer separated. The aqueous layer was extracted with chloroform (2 × 20 ml.) and the combined organic extracts dried and the solvent removed. An ethereal solution of the residue was chromatographed on silica and eluted with more ether and the *product* so obtained sublimed at 80°/0·1 mm. to give yellow prisms (124 mg., 28·5%), m. p. 108—109·5° (Found: C, 68·5; H, 5·9. $C_{11}H_{12}O_3$ requires C, 68·7; H, 6·3%), $\lambda_{max.}$ 233, 280, 335, and 377 mμ (ε 5540, 38,300, 6150, and 8020, respectively), and in aqueous sodium hydroxide, $\lambda_{max.}$ 230 and 295 with an inflection at 335 mμ; $\nu_{max.}$ 1581, 1617, and 1673 (ε 589) cm.$^{-1}$. The n.m.r. spectrum showed peaks at τ −8·58 (s; hydroxyl proton), 2·32 (s; nuclear protons), 7·40 and 7·63 (s; *C*-methyl groups).

2-*Acetyl-α-hydroxy-3,α-dimethylfulvene* (XIII; R = H, R′ = Me).—Methylcyclopentadiene (8·0 g.) was converted to the sodio-derivative with sodium hydride (2·4 g.) in dry tetrahydrofuran (50 ml.). Redistilled acetyl chloride (7·85 g.) in tetrahydrofuran (10 ml.) was added dropwise at 0° over 30 min. after which the stirring was continued for a further hour at 0°, and then the temperature was raised to 25° during 30 min. The mixture was then poured into water (350 ml.) and extracted with ether (3 × 30 ml.). The aqueous layer was acidified with hydrochloric acid and re-extracted with ether. The combined ethereal extracts were washed with water (4 × 100 ml.) and dried ($MgSO_4$). After removal of the solvent, the residual oil was distilled rapidly at 13 mm. and the distillate b. p. >135° was collected in several fractions and each treated with a small amount of methanol and kept at 0° to induce crystallisations. Two crude products were thus obtained, m. p. 45—50 and 75—80°, respectively. Repeated crystallisation of the former gave 2-*acetyl-α-hydroxy-3,α-dimethylfulvene* as yellow needles (30 mg.), m. p. 52·5—53·5° [Found: C, 73·5; H, 7·4%; *M* (mass spectroscopy), 164. $C_{10}H_{12}O_2$ requires C, 73·15; H, 7·35%; *M*, 164], $\lambda_{max.}$ 249, 331, and 393 mμ (ε 17,300, 12,400, and 8850, respectively) and in ethanolic sodium hydroxide, $\lambda_{max.}$ 251·5, 339, and 375·5 mμ; $\nu_{max.}$ 1570 cm.$^{-1}$. The n.m.r. spectrum showed resonances at τ −8·57 (s; hydroxyl proton), 2·80, 3·82 (both d; $J$ = 4 c./sec.; nuclear protons), 7·44 and 7·50 (both s; 3 *C*-methyls, 2 superimposed).

The higher melting product was crystallised repeatedly from methanol and then was sublimed at 60°/0·1 mm. when it was obtained as yellow plates, m. p. 79—82°; $\nu_{max.}$ 1576 cm.$^{-1}$; [*M* (mass spectroscopy), 164. $C_{10}H_{12}O_2$ requires *M*, 164.] The n.m.r. spectrum showed resonances at τ −7·76 (s; hydroxyl proton), 2·97 (s; nuclear protons), 7·50 (s; acetyl protons and 6-methyl group), and 7·85 (s; 3-methyl group). This product was therefore the isomeric 2-acetyl-α-hydroxy-4,α-dimethylfulvene (XIII; R = Me, R′ = H).

We acknowledge the award of a Maintenance Grant from the S.R.C. (to R. F. C.).

[6/789 *Received, June 24th,* 1966]