#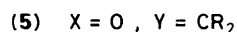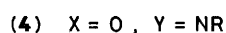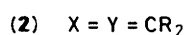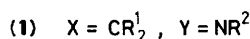 Thermolysis of Polyazapentadienes. Part 11.[1] Concerted and Free Radical Mechanisms in 2-Aza Enone and 2-Aza Enthione Pyrolyses: Crystal and Molecular Structures of 3-Dimethylamino-1-*p*-tolyl-2-azaprop-2-en-1-one and 3-Dimethylamino-1-phenyl-2-azaprop-2-ene-1-thione

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Flash vacuum pyrolysis of the dimethylamino-azapropenones (7)—(9) and -azapropenethione (12) gives nitriles and amides (or thioamide) in yields of *ca.* 30% by an electrocyclisation-ring cleavage mechanism. This is a minor pathway for the triarylazapropenones (14) and (15) for which homolytic cleavage of the C–N bond gives rise to the major products. The *X*-ray crystal structures of (10) and (12) show that the conjugated systems are almost planar in the *s-Z* conformation, as required for the electrocyclic ring closure.

The work described in the previous paper[1] explores the thermal cleavage of HCN from the central atoms of an azoalkene unit (1). The terminal nitrogen atom is apparently not necessary for this behaviour, since there is considerable evidence that 2-aza dienes (2) can decompose by a similar mechanism,[2] and that other terminal hetero-atoms can also become involved *e.g.* (3).[3] However, alternative free-radical cleavage may be observed, *e.g.* (4).[1] An extension of these ideas to 2-aza enones (5) and 2-aza enethiones (6) is now described, in which the interpretation of the pyrolysis results is reinforced by *X*-ray crystallographic studies of typical precursors.

(1)   X = CR$_2^1$, Y = NR^2

(2)   X = Y = CR$_2$

(3)   X = CR$_2$, Y = O

(4)   X = O , Y = NR

(5)   X = O , Y = CR$_2$

(6)   X = S , Y = CR$_2$
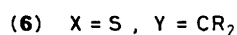
By analogy with the azoalkene work, in which 'push-pull' substituents on the conjugated system gave particularly satisfactory results, we synthesized the dimethylaminoaza-propenones (7)—(10). The alkyl- and aryl-substituted examples (8)—(10) were readily prepared by the action of the corresponding alkyl- or aryl-amide on dimethylformamide diethyl acetal in dioxane at 80 °C.[4] The corresponding reaction with

(7)   R = H
(8)   R = Me
(9)   R = Ph
(10) R = *p* - tolyl
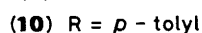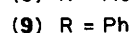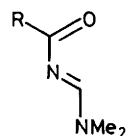
formamide itself, however, caused disproportionation to dimethylformamide and ethanol (and, presumably, HCN), though the required product (7) could be prepared[5] from bis-dimethylamino-t-butoxymethane[6] which is a highly reactive dimethylaminomethylenating agent. The thione[7] (12) was also readily obtained (62%) from thiobenzamide under the standard conditions,[4] though the methyl-substituted analogue (11) was not obtained from thioacetamide, further reaction taking place at the *C*-methyl group to give (13).[8]

(11) R = Me
(12) R = Ph

(13)
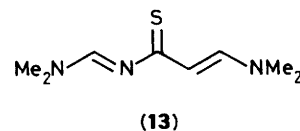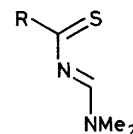
Because of their poor hydrolytic stability, the only examples lacking amino substitution which were studied in these series were the triaryl derivatives (14) and (15), obtained from the reaction of benzophenone imine with the appropriate aroyl chloride.[9] Some simpler derivatives have been made by flash pyrolysis methods[10,11] and are thermally stable to at least 600 °C.

(14) R = Ph
(15) R = *p* - tolyl
(16) R = Me
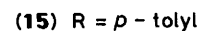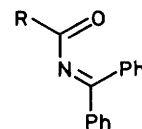
The mass spectra of compounds (7)—(10) and (12) are unexceptional, and bear little relation to the anticipated thermal breakdown. Ionisation at the (thio)carbonyl group is followed

by competitive cleavage of the adjacent C–C and C–N bonds [*e.g.* (9); $M − Ph$, m/z 99 (100%); $M − Me_2NCHN$, m/z 105 (81%)]. The triaryl derivatives (14) and (15) show a similar pattern, though C–N cleavage assumes greater importance [*e.g.* (15); $M − Ar$, m/z 208 (5%); $M − Ph_2CN$, m/z 119 (100%).].

The azapropenones (7)—(9) are significantly more thermally stable than the azo compounds described in the previous paper,[1] though at 900 °C low yields of nitriles (20—35%) and amides (7—30%) were obtained, which can be explained by an analogous mechanism *via* the four-membered ring intermediate (17) (Scheme 1). It is possible that the extreme conditions may

Scheme 1.
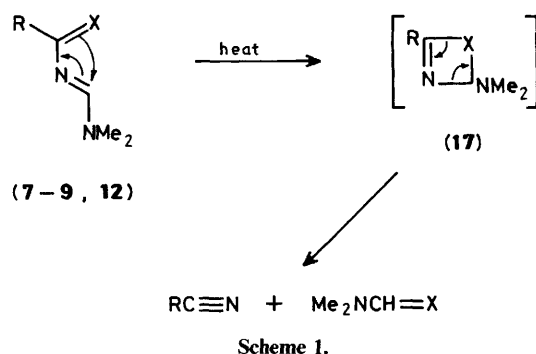
be partially responsible for the low yields, since degradation to volatile (and hence undetected) components may compete with the electrocyclisation. However, secondary decomposition of the products is unlikely since a control experiment established that dimethylformamide is recovered unchanged at 900 °C. The particularly low level of dimethylformamide (7%) in the pyrolysis of the *C*-unsubstituted compound (7) is noteworthy, and contrasts with the higher yields of both the amide and nitrile products (Scheme 1) which were obtained by pyrolysis of the thione (12) at 900 °C. The increased size and polarisability of the sulphur atom may promote the intramolecular bonding to give (17). Indeed, examples of the 2*H*-1,3-thiazete ring system are known as isolable compounds,[12] though both these and their oxygen analogues can behave as the ring-opened valence isomers.[13,14]

Thermal cleavage of the triphenyl compound (14) by the mechanism of Scheme 1 would give benzonitrile and benzophenone, and indeed both products were obtained in the 900 °C pyrolysate (54 and 15% respectively) [Scheme 2, route (a)]. However, biphenyl (5%) was also detected; this was shown by a control experiment *not* to arise by secondary breakdown of benzophenone and its presence therefore suggests that a free radical mechanism might be involved. Though the yield of the coupled product is low, it is certainly significant in view of the poor dimerization efficiency of phenyl radicals.[1,15] The most likely source of these radicals [Scheme 2, route (b)] is *via* homolysis of the C–N bond to give aroyl and diphenyliminyl species (18) and (19), followed by further fragmentation: cleavage of CO from (18) is expected at 900 °C,[1,16] and β-cleavage of iminyl radicals is well known when these are generated by azine pyrolysis.[17,18] Since the radical mechanism also gives rise to 1 equiv. of benzonitrile, it is not clear from this example whether both mechanisms of Scheme 2 are operating, or whether, for example, the benzophenone arises by adventitious hydrolysis of the precursor. This ambiguity was removed by a study of the *p*-tolyl derivative (15) since *different* nitriles are formed by the electrocyclic [route (a)] and free radical [route (b)] pathways (Scheme 2). Analysis of the pyrolysate by g.l.c. showed that the ratio of *p*-toluonitrile : benzonitrile was 1:18, *i.e.* less than 6% of the reaction followed the
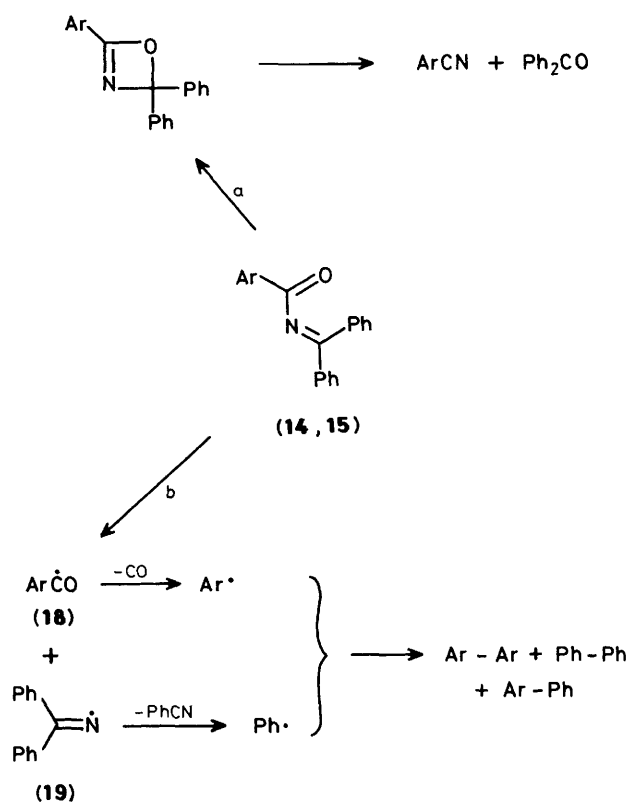
Scheme 2.

electrocyclisation pathway. The expected 'cross-over' biaryls were also identified (Scheme 2), together with a slightly higher level of benzophenone than expected, which suggests that some accidental hydrolysis may indeed have taken place.

In general terms, therefore, the 'push-pull' derivatives (7)—(9) and (12) undergo electrocyclisation [though the low yields from (7) are anomalous] whereas the triaryl derivatives (14) and (15) undergo free radical cleavage. We were attracted by a possible structural explanation of this behaviour, since an expected resonance form (7—12A) lies on the reaction co-ordinate to the intermediate (17), whereas the azapropenones (16)[19] and (20)[20] are known to be non-planar. Accordingly, we have carried out *X*-ray structure determinations of the crystalline 'push-pull' derivatives (10) and (12).

(20)   (7 – 12 A)
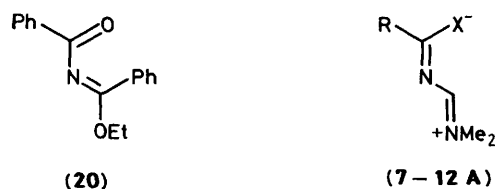
Bond lengths, angles and fractional co-ordinates of (10) and (12) are given in Tables 1—4 and 5—8 respectively and the important features are summarised in Figure 1. ORTEP views of both molecules, showing the crystallographic numbering systems, are shown in Figure 2, while the published[19,20] data for the model compounds (16) and (20) are given in Figure 3.

The most notable feature of the structures of (10) and (12) is that they adopt the s-*Z* conformation, and that only slight deviations from planarity are observed. Incipient formation of the intermediate (17) is not supported by the ground state structures, since the N(2)–C(3)–N(4)–Me units are almost planar.
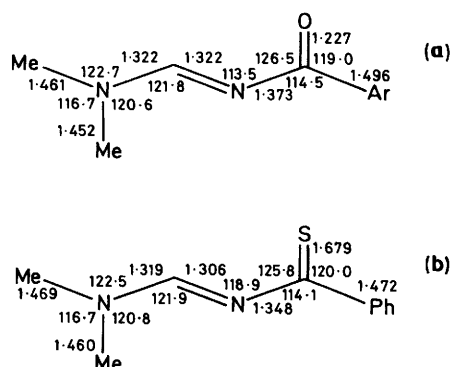
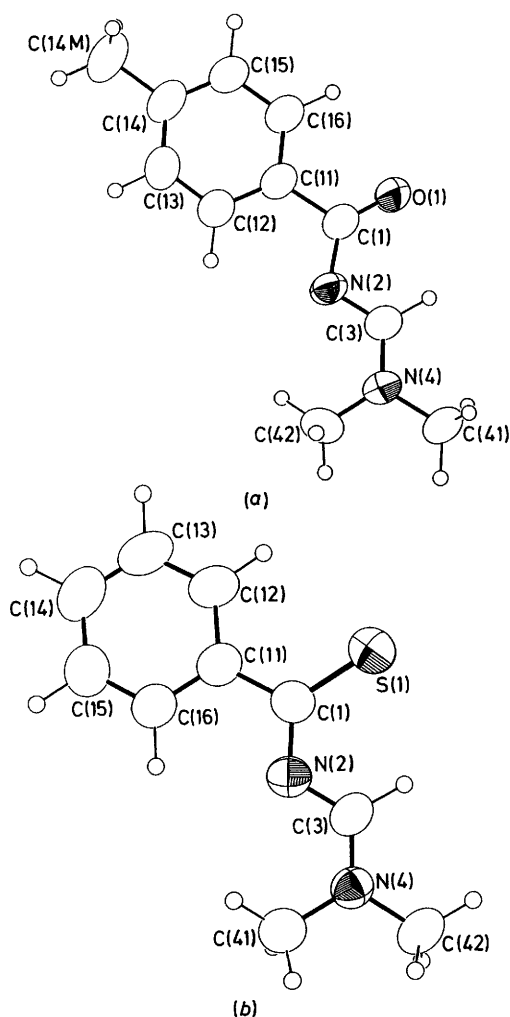**Figure 1.** Selected bond lengths (Å) and angles (°) of (a) (10) and (b) (12)

Figure 2. ORTEP views of (a) (10) and (b) (12) showing crystallographic numbering scheme
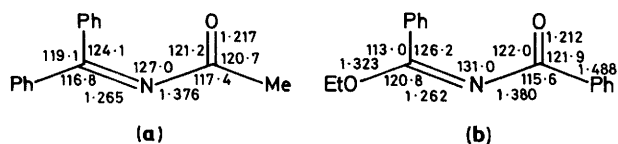

Figure 3. Selected bond lengths (Å) and angles (°) of (a) (16) and (b) (20)

In view of the expected 'push-pull' nature of the conjugation in (10) which is not present in the model compound (16), the similarity of the bond lengths in the O(1)–C(1)–N(2) region of the molecules is remarkable: the C–N and C–O distances [in (10) and (16)] are within one standard deviation of each other as is the C(1)–Ar bond length [in (10) and (20)]. Though the length of the C(1)–O(1) bond is close to that expected of a typical amide, the C(1)–N(1) bond is rather longer.[21] Clearly electron density from the (4)-amino group is not reaching the carbonyl function, and so these dialkyl-aminoazapropenes are perhaps best regarded simply as acylated amidines. This interpretation is supported by the symmetry of the N(2)–C(3) and C(3)–N(4) bond lengths in (10), and by the degree of partial bond character reflected in these distances being significantly longer than the C=N bond in both (16) and (20), despite possible electron donation from the ethoxy group in the latter case. These parameters are slightly—but not significantly—distorted in the thione (12): both the C(1)–N(2) and the C(1)–Ar bonds are also slightly shorter than in the oxygen analogue (10) (> 2 standard deviations), consistent with electron density being transmitted to the sulphur atom. The C–S bond length (1.679 Å) is of the same order as in thioamides.[22] One feature in which the structures of (10) and (12) are spectacularly different from (16) and (20) is the dihedral angle of the C=N–C=X unit, which is, respectively, −4.3(5)°, −8.0(7)°, 73.0(7)°, and −71.6(5)°. Involvement of dipolar canonical forms (21), in which the lone pair of the 'aza'-nitrogen atom takes part

(21)
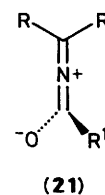
in the conjugation has been considered[19] to explain the almost orthogonal nature of the π-systems in (16) and (20) and in agreement with this, the C(1)–N(2)–C(3) angle (127.0° and 131.0° respectively) is considerably wider than in our examples [(10), 113.5°; (12), 118.9°].

Although the nature of the conjugation in (10) and (12) is perhaps rather unexpected, the s-Z planar conformation of the ground state allows the terminal atoms of the heterodiene to be correctly positioned for electrocyclisation. It is known from studies of related enaminones,[23] that the conformation of these systems can be strongly dependent on the nature of substituents in the 1-position, and indeed we have shown that the iminium salt (22) adopts the s-E conformation in the solid state.[24] An

(picrate)⁻
(22)
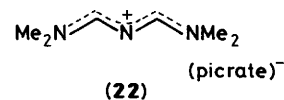
n.O.e. difference study of the 1-methyl derivative (8) showed no enhancement of the 3-proton on irradiation of the 1-methyl group, which confirms that the s-Z geometry is maintained. However, enhancements at the 1- and 3-protons of (7) of 12—14% were observed on irradiation of the 3- and 1-proton signals respectively, and so the ground state of the C-unsubstituted system is s-E as found in the enaminone series.

Though the energy differences for rotation about the C–N bond in these systems are not likely to be great[19,20] we nevertheless believe that these results allow a consistent explanation of the thermolysis behaviour. The electrocyclic

pathway (Scheme 1 and Scheme 2a) requires a planar s-Z geometry of the aza enone system for orbital overlap. Considering the entropy factor at 900 °C, this is most likely when it corresponds closely to the ground state of the molecule, as in (8), (10), and (12) [and by implication, (9)]. This route is therefore much less efficient for the parent compound (7) which has an s-E structure. Radical cleavage has no geometric constraints and therefore is the dominant reaction pathway for (14) and (15), where the equilibrium conformation is likely to be far from planar.

In conclusion, we have shown in this, and the previous paper,[1] that despite competing radical reactions, thermal 4π-electron electrocyclic ring closure followed by elimination of RCN can apply to a wide variety of heterodiene systems [cf. (1)—(6)] in which one of the central atoms is nitrogen. In a wider context, Wendling and Bergman's original observations[2] in the 2-aza-alkene series have been substantiated by further observations by Govindan and Taylor,[25] and by Ripoll and co-workers.[26] The parent azetine (23) is known to undergo thermal ring-opening to the aza diene,[27] but under conditions (450 °C and 10^{-4} Torr) at which cleavage to ethylene and HCN would not be expected.


(23)

Systems with heteroatoms in the 1-position which thermolyse by an electrocyclisation-cleavage pathway include the azoalkenes[1,28,29] reported in the previous paper, and nitroso alkenes[3] (24) which may also be generated *in situ*.[30–32] It is of interest that systems with heteroatoms in the 3-position (e.g. azines) normally undergo radical cleavage,[18] though considerable work on loss of N_2 from N-nitroso-ketimines[33–35] (25) is consistent with an electrocyclic ring closure mechanism. Finally, the presence of *any* heteroatom in the 2- and 3-positions of a diene system may be superfluous in special cases, and it has been proposed that acetylenes may arise by a similar mechanism in the silene series (Scheme 3).[36,37]

(24)   **(25)**

X = O, S

[Me₂Si=X] + Me₃SiC≡CH
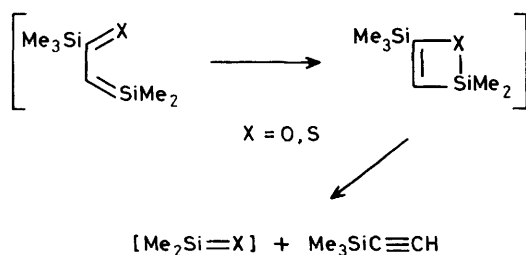
Scheme 3.

Experimental

¹H N.m.r. spectra were recorded at 80 or 200 MHz, and ¹³C n.m.r. spectra at 20 or 50 MHz, for solutions in [²H]chloroform.

3-Dimethylamino-2-azaprop-2-en-1-ones.[4]—The appropriate amide (0.05 mol) was mixed with N,N-dimethylformamide diethyl acetal (0.075 mol) and dioxane (10 g), and the mixture heated at 80 °C for 2 h. The ethanol formed and unchanged

dioxane were removed under reduced pressure and the product was purified either by distillation or recrystallisation. The following compounds were made by this method. 3-Dimethyl-amino-1-methyl-2-azaprop-2-en-1-one (8) (91%) (from acetamide), b.p. 71 °C (0.4 Torr) [lit.,[4] 60 °C (0.25 Torr)]; $v_{max.}$ 1 650 cm⁻¹ (CO); δ_H 8.09 (1 H, s), 2.86 (3 H, s), 2.79 (3 H, s), and 1.87 (3 H, s); δ_C 184.06 (q), 159.40, 40.76, 23.59, and 26.46; m/z 114 (M^+, 41%), 99 (100), and 43 (33); 3-dimethylamino-1-phenyl-2-azaprop-2-en-1-one (9) (93%) from benzamide, m.p. 75—76 °C (from ether) (lit.,[4] 67—69 °C); $v_{max.}$ 1 650 cm⁻¹ (CO); δ_H 8.42 (1 H, s), 8.2—8.1 (2 H, m), 7.35—7.15 (3 H, m), 2.91 (3 H, s), and 2.83 (3 H, s); δ_C 177.43 (q), 160.44, 136.62 (q), 131.55, 129.49, 127.66, 41.02, and 34.97; m/z 176 (M^+, 58%), 105 (81), 99 (100), and 77 (84); 3-dimethylamino-1-p-tolyl-2-azaprop-2-en-1-one (10) (70%), from p-toluamide, m.p. 89—90 °C (from ether) (Found: C, 69.2; H, 7.55; N, 14.6. $C_{11}H_{14}N_2O$ requires C, 69.45; H, 7.35; N, 14.75%); $v_{max.}$ 1 640 cm⁻¹ (CO); δ_H 8.58 (1 H, s), 8.14 (2 H, d), 7.18 (2 H, d), 3.15 (3 H, s), 3.11 (3 H, s), and 2.36 (3 H, s); δ_C 177.47 (q), 160.33, 141.95 (q), 134.12 (q), 129.68, 128.42, 40.92, 34.95, and 20.30; m/z 190 (M^+, 53%), 119 (100), 99 (59), 91 (50), 71 (16), and 65 (22).

3-Dimethylamino-2-azaprop-2-en-1-one (7).—An attempted preparation using a mixture of formamide (4.5 g, 0.1 mol) and N,N-dimethylformamide diethyl acetal in dioxane (20 g) at 80 °C (2 h) gave a mixture which was shown by ¹H n.m.r. spectroscopy, g.c. and g.c./m.s. to consist only of dimethyl-formamide and ethanol in dioxane.

A mixture of bisdimethylamino-t-butoxymethane (2.0 g, 12 mmol) and formamide (0.40 g, 9 mmol) was stirred at room temperature. After 5 min, the solution became homogeneous, and after 40 min it was distilled (Kugelrohr) under reduced pressure. The fraction boiling at 101—103 °C (0.1 Torr) [lit.,[38] 154 °C (13 Torr)] was essentially pure azapropenone (0.26 g, 29%); $v_{max.}$ 1 690 and 1 600 cm⁻¹; δ_H 8.88 (1 H, s), 7.94 (1 H, s), 3.07 (3 H, s), and 2.99 (3 H, s); δ_C 176.16, 166.38, 41.11, and 35.38; m/z 100 (M^+, 87%), 99 (100), 72 (18), and 44 (78).

3-Dimethylamino-1-phenyl-1-azaprop-2-ene-1-thione (12).—A mixture of thiobenzamide (10 g, 0.07 mol) and N,N-dimethylformamide diethyl acetal (35 g, 0.23 mol) was heated for 1 h at 50 °C. The ethanol formed during the course of the reaction was then removed under reduced pressure and the residue was filtered off and washed with ether to give a red solid (8.65 g, 62%), m.p. 57—59 °C (lit.,[4] 50—54 °C); $v_{max.}$ 965 cm⁻¹ (CS); δ_H 8.73 (1 H, s), 8.5—8.35 (2 H, m), 7.5—7.25 (3 H, m), and 3.23 (6 H, apparent s); δ_C 215.48 (q), 158.73, 142.79 (q), 131.46, 128.50, 127.29, 41.49, and 35.98; m/z 192 (M^+, 39%), 159 (43), 121 (100), and 115 (39).

Attempted Preparation of 3-Dimethylamino-1-methyl-2-azaprop-2-ene-1-thione (11).—A mixture of thioacetamide (3.75 g, 25 mmol) and N,N-dimethylformamide diethyl acetal (7.35 g, 25 mmol) was heated for 1 h at 50 °C. The ethanol formed was evaporated under reduced pressure before the remaining semisolid was triturated with ether. The crystals which formed were filtered off, washed with cyclohexane and dried to give a brown solid (2.04 g), m.p. 150 °C (from ethanol); δ_H 8.82 (1 H, s), 8.19 (1 H, d), 5.88 (1 H, d), 3.11 (6 H, s), and 3.08 (6 H, s); m/z 185 (M^+, 96%), 152 (17), 130 (100), 114 (30), 97 (30), and 82 (30). The ¹H n.m.r. spectrum and m.s. suggest that the compound formed is the N-(3-aminothioacryloyl)formamidine (13). This compound has been prepared by Liebscher[8] using a similar method.

1-Aryl-3,3-diphenyl-2-azaprop-2-en-1-ones (9).—Benzophen-one imine[39] (0.05 mol) was added to a solution of the appropriate aroyl chloride (0.057 mol) in pyridine (20 g), and

the mixture was warmed on a water-bath for *ca.* 2 h. The cooled mixture was then poured onto water (500 ml), weakly acidified with hydrochloric acid, and the 1-aryl-3,3-diphenyl-2-azaprop-2-en-1-one was filtered off and dried *in vacuo* over phosphorus pentaoxide. The following compounds were prepared in this way. 1,3,3-Triphenyl-2-azaprop-2-en-1-one (**14**) (99%), m.p. 110—111 °C (lit.,[9] 117—118 °C); $\nu_{max.}$ 1 660 cm^{-1} (CO); δ_H 7.7—6.9 (15 H, m); δ_C 178.98 (q), 167.47 (q), and overlapping benzenoid signals in the range 128—136; *m/z* 285 (M^+, 49%), 105 (100), 77 (72), and 51 (29). 3,3-*Diphenyl*-1-p-*tolyl*-2-*azaprop*-2-*en*-1-*one* (**15**) (100%), m.p. 155—157 °C (from ethanol) (Found: C, 84.1; H, 5.85; N, 4.6. $C_{21}H_{17}NO$ requires C, 84.25; H, 5.7; N, 4.7%); $\nu_{max.}$ 1 660 cm^{-1} (CO); δ_H 8.1—7.1 (14 H, m) and 2.34 (3 H, s); δ_C 179.06 (q), 167.29 (q), 143.31 (q), 136.39 (q), overlapping benzenoid signals in the range 128—131, and 21.39; *m/z* 299 (M^+, 43%), 119 (100), 91 (47), 77 (24), and 51 (11). These compounds were particularly prone to hydrolysis, and were normally stored at -20 °C.

Pyrolysis Experiments.—General pyrolysis techniques and analytical methods were described in the previous paper.[1] Parameters for small-scale pyrolyses are quoted as follows: substrate, inlet temperature, furnace temperature, pressure, pyrolysis time, and products.

(i) *Dimethylamino-azapropenones and -azapropenethiones.* (a) 3-*Dimethylamino-1-methyl-2-azaprop-2-en-1-one* (**8**) (0.152 g, 1.33 mmol); 70 °C; 900 °C; 5 × 10^{-3} Torr; 60 min; *N,N*-dimethylformamide (29%) *m/z* 73; acetonitrile (24%) (this was clearly shown to be present by ^{1}H n.m.r. spectroscopy and by g.c. comparison with an authentic sample. However, under g.c./m.s. conditions the peak was too close to the solvent for resolution); dimethylacetamide (trace) *m/z* 87; *N,N*-dimethyl-cyanamide (trace) was tentatively identified due to the presence of the correct molecular ion in the g.c./m.s., *m/z* 70.

(b) 3-*Dimethylamino-1-phenyl-2-azaprop-2-en-1-one* (**9**) (0.085 g, 0.483 mmol); 140 °C; 900 °C; 5 × 10^{-3} Torr; 60 min; *N,N*-dimethylformamide (30%) *m/z* 73; benzonitrile (35%) *m/z* 103.

(c) 3-*Dimethylamino-2-azaprop-2-en-1-one* (**7**) (0.045 g, 0.45 mmol); 55 °C; 900 °C; 5 × 10^{-3} Torr; 30 min; *N,N*-dimethyl-formamide (7%) *m/z* 73: a number of other components (<5% level) were detected by g.l.c., but were not identified.

(d) 3-*Dimethylamino-1-phenyl-2-azaprop-2-ene-1-thione* (**12**) (0.175 g, 0.91 mmol); 140—160 °C; 900 °C; 3 × 10^{-3} Torr; 45 min; *N,N*-dimethylthioformamide (35%) *m/z* 89; benzonitrile (65%) *m/z* 103.

Pyrolysis of dimethylformamide (0.154 g, 2.11 mmol); 40—60 °C; 900 °C; 8 × 10^{-3} Torr; 45 min: the pyrolysate was shown by ^{1}H n.m.r. spectroscopy and g.c. to be unchanged starting material.

(ii) *Triarylazapropenones.* A number of problems were encountered with these pyrolyses. First, the lowest pyrolysis temperature at which the substrate was totally consumed could not be determined by our normal methods because the starting materials had no distinguishing n.m.r. spectroscopic features, and were not eluted by g.l.c. However, the comparatively low solubility of the *p*-methyl compound in chloroform was a useful gauge: at furnace temperatures below 900 °C, such solid in the pyrolysate was shown (m.p. and m.s.) to be recovered starting material. Second, the detection of benzophenone in the pyrolysate has no mechanistic significance since it is inevitably formed by some hydrolysis of the starting material, probably in the pyrolysis inlet system.

(a) 1,3,3-*Triphenyl-2-azaprop-2-en-1-one* (**14**) (0.134 g, 0.47 mmol); 140—160 °C; 900 °C; 5 × 10^{-3} Torr; 30 min: benzo-nitrile (54%) *m/z* 103; benzophenone (15%) *m/z* 182; biphenyl (5%) *m/z* 154.

(b) 3,3-*Diphenyl*-1-p-*tolyl-2-azaprop-2-en-1-one* (**15**) (0.309 g,

1.09 mmol); 160 °C; 900 °C; 5 × 10^{-3} Torr; 45 min: benzo-nitrile (71%) *m/z* 103; *p*-toluonitrile (4%) *m/z* 117; biphenyl (3%) *m/z* 154; 4-methylbiphenyl (2%) *m/z* 168; 4,4′-dimethyl-biphenyl (2%) *m/z* 182; benzophenone (6%) *m/z* 182.

In the above experiments, a significant amount of a colourless liquid was present in the trap, which is almost certainly benzene (and/or toluene), formed by hydrogen capture of the aryl radicals (*cf.* ref. 1).

Pyrolysis of benzophenone (0.309 g, 1.70 mmol), 100 °C; 900 °C; 4 × 10^{-3} Torr; 45 min: the pyrolysate was shown by g.c. comparison with an authentic sample to be unchanged starting material.

Crystal Data.—Compound (**12**) $C_{10}H_{12}N_2S$, $M = 192.28$, monoclinic, space group $P2_1/c$, $a = 6.2514(14)$, $b = 21.929(8)$, $c = 7.9911(19)$ Å, $\beta = 107.434(17)°$, $V = 1 045.2$ Å^3 (by least-squares refinement on diffractometer angles for 14 centred reflections with $\theta = 20—25°$, $\lambda = 1.54184$ Å), $T = 298$ K, $Z = 4$, $D_c = 1.222$ g cm^{-3}. Dark red, acicular crystal, $0.55 × 0.20 × 0.10$ mm, $F(000) = 408$, $\mu(Cu-K_\alpha) = 22.68$ cm^{-1}.

Data Collection and Processing.—Stoe-Siemens AED2 four-circle diffractometer, ω–2θ scans with ω scan width (1.05 + 0.348 tan θ)°, $T = 298$ K, graphite-monochromated Cu-K_α X-radiation; 1 648 reflections measured (2$\theta_{max.} = 120°$, $\pm h$, $+k$, $+l$), 1 465 unique ($R_{int.} = 0.0403$), giving 1 289 with $F > 6\sigma(F)$, no significant crystal decay or movement.

Structure Solution and Refinement.—Patterson synthesis (S) followed by iterative rounds of least-squares refinement and difference Fourier synthesis located all non-hydrogen atoms. At isotropic convergence, empirical absorption correction[40] applied (max. and min. corrections 1.452, 0.542 respectively). Full-matrix least-squares refinement (F) with H atoms in calculated positions[41] converged to $R,R_w = 0.0842, 0.0754$ respectively. Unit weights gave satisfactory agreement analyses, max. and min. residues in the final difference Fourier synthesis were $+0.29$ and -0.57 eÅ^{-3} respectively, S = 1.021.

Crystal Data.—Compound (**10**) $C_{11}H_{14}N_2O$, $M = 190.24$, monoclinic, space group $P2_1/n$, $a = 7.1786(21)$, $b = 10.029(3)$, $c = 14.968(4)$ Å, $\beta = 96.393(23)°$, $V = 1 070.9$ Å^3 (by least-squares refinement on diffractometer angles for 16 centred reflections with $\theta = 17—24°$, $\lambda = 1.541 84$ Å), $T = 298$ K, $Z = 4$, $D_c = 1.180$ g cm^{-3}. Colourless, lamellar crystal, $0.62 × 0.62 × 0.30$ mm, $F(000) = 408$, $\mu(Cu-K_\alpha) = 5.41$ cm^{-1}.

Data Collection and Processing.—Stoe-Siemens AED2 four-circle diffractometer, ω–2θ scans using the learnt profile method,[42] $T = 298$ K, graphite-monochromated Cu-K_α X-radiation; 2 337 reflections measured (2$\theta_{max.} = 120°$, $\pm h$, $\pm k$, $+l$), 1 425 unique ($R_{int.} = 0.0383$), giving 1 230 with $F > 6 \sigma(F)$, no significant crystal decay or movement.

Structure Solution and Refinement.—Automatic direct methods[43] found all non-hydrogen atoms. Full-matrix least-squares refinement (F) with H atoms in calculated positions[41] converged to $R,R_w = 0.0690, 0.0901$ respectively. The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses, max. and min. residues in the final difference Fourier synthesis were $+0.17$ and -0.20 e Å^{-3} respectively, S = 0.959. A secondary extinction parameter refined to $0.213(14) × 10^{-4}$. Molecular geometry calculations were performed using CALC:[44] Figures were produced from ORTEP;[45] selected molecular geometry parameters are listed in Tables 1—3 and 5—7, and refined fractional co-ordinates in Tables 4 and 8. Thermal parameters, calculated H atom positions and structure factors have been deposited. Full structural parameters are

Table 1. Bond lengths (Å) with standard deviations of (10)

O(1)–C(1)	1.227(4)	C(11)–C(12)	1.383(4)
C(1)–N(2)	1.373(4)	C(11)–C(16)	1.388(5)
C(1)–C(11)	1.496(4)	C(12)–C(13)	1.388(5)
N(2)–C(3)	1.322(4)	C(13)–C(14)	1.385(5)
C(3)–N(4)	1.322(4)	C(14)–C(15)	1.365(5)
N(4)–C(41)	1.461(5)	C(14)–C(14M)	1.511(5)
N(4)–C(42)	1.452(4)	C(15)–C(16)	1.386(5)

Table 2. Angles (°) with standard deviations of (10)

O(1)–C(1)–N(2)	126.5(3)
O(1)–C(1)–C(11)	119.0(3)
N(2)–C(1)–C(11)	114.5(3)
C(1)–N(2)–C(3)	113.5(3)
N(2)–C(3)–N(4)	121.8(3)
C(3)–N(4)–C(41)	120.6(3)
C(3)–N(4)–C(42)	122.7(3)
C(41)–N(4)–C(42)	116.7(3)
C(1)–C(11)–C(12)	122.5(3)
C(1)–C(11)–C(16)	119.1(3)
C(12)–C(11)–C(16)	118.4(3)
C(11)–C(12)–C(13)	120.0(3)
C(12)–C(13)–C(14)	121.8(3)
C(13)–C(14)–C(15)	117.6(3)
C(13)–C(14)–C(14M)	122.1(3)
C(15)–C(14)–C(14M)	120.3(3)
C(14)–C(15)–C(16)	121.8(3)
C(11)–C(16)–C(15)	120.4(3)

Table 3. Torsion angles (°) with standard deviations of (10)

O(1)–C(1)–N(2)–C(3)	−4.3(5)
C(11)–C(1)–N(2)–C(3)	177.9(3)
O(1)–C(1)–C(11)–C(12)	177.6(3)
O(1)–C(1)–C(11)–C(16)	−1.8(5)
N(2)–C(1)–C(11)–C(12)	−4.5(4)
N(2)–C(1)–C(11)–C(16)	176.2(3)
C(1)–N(2)–C(3)–N(4)	178.0(3)
N(2)–C(3)–N(4)–C(41)	−179.2(3)
N(2)–C(3)–N(4)–C(42)	2.1(5)
C(1)–C(11)–C(12)–C(13)	179.6(3)
C(16)–C(11)–C(12)–C(13)	−1.1(5)
C(1)–C(11)–C(16)–C(15)	−179.0(3)
C(12)–C(11)–C(16)–C(15)	1.6(5)
C(11)–C(12)–C(13)–C(14)	0.4(5)
C(12)–C(13)–C(14)–C(15)	−0.3(5)
C(12)–C(13)–C(14)–C(14M)	−179.0(3)
C(13)–C(14)–C(15)–C(16)	0.9(5)
C(14M)–C(14)–C(15)–C(16)	179.6(3)
C(14)–C(15)–C(16)–C(11)	−1.6(5)

Table 4. Fractional co-ordinates of atoms with standard deviations of (10)

Atom	x	y	z
O(1)	0.192 3(4)	0.560 12(24)	0.943 99(17)
C(1)	0.179 8(4)	0.668 2(3)	0.905 37(22)
N(2)	0.049 1(3)	0.765 62(23)	0.914 99(16)
C(3)	−0.078 5(4)	0.730 2(3)	0.967 68(20)
N(4)	−0.212 1(3)	0.812 8(3)	0.986 73(16)
C(41)	−0.349 7(5)	0.771 3(4)	1.046 1(3)
C(42)	−0.233 2(4)	0.946 2(4)	0.949 26(24)
C(11)	0.321 7(4)	0.704 0(3)	0.843 38(20)
C(12)	0.313 4(4)	0.821 6(3)	0.794 90(21)
C(13)	0.449 8(5)	0.849 9(4)	0.738 86(22)
C(14)	0.595 8(5)	0.762 7(4)	0.729 21(22)
C(15)	0.602 0(5)	0.647 0(4)	0.777 38(25)
C(16)	0.466 7(5)	0.615 7(3)	0.833 19(24)
C(14M)	0.746 6(5)	0.793 7(4)	0.669 5(3)

Table 5. Bond lengths (Å) with standard deviations of (12)

S(1)–C(1)	1.679(5)	C(11)–C(12)	1.406(8)
C(1)–N(2)	1.348(7)	C(11)–C(16)	1.398(8)
C(1)–C(11)	1.472(7)	C(12)–C(13)	1.369(9)
N(2)–C(3)	1.306(7)	C(13)–C(14)	1.374(10)
C(3)–N(4)	1.319(7)	C(14)–C(15)	1.386(10)
N(4)–C(41)	1.460(8)	C(15)–C(16)	1.366(9)
N(4)–C(42)	1.469(8)		

Table 6. Angles (°) with standard deviations of (12)

S(1)–C(1)–N(2)	125.8(4)	C(1)–C(11)–C(12)	122.0(5)
S(1)–C(1)–C(11)	120.0(4)	C(1)–C(11)–C(16)	120.6(5)
N(2)–C(1)–C(11)	114.1(4)	C(12)–C(11)–C(16)	117.4(5)
C(1)–N(2)–C(3)	118.9(5)	C(11)–C(12)–C(13)	120.9(5)
N(2)–C(3)–N(4)	121.9(5)	C(12)–C(13)–C(14)	121.4(6)
C(3)–N(4)–C(41)	120.8(5)	C(13)–C(14)–C(15)	117.7(6)
C(3)–N(4)–C(42)	122.5(5)	C(14)–C(15)–C(16)	122.2(6)
C(41)–N(4)–C(42)	116.7(5)	C(11)–C(16)–C(15)	120.2(5)

Table 7. Torsion angles (°) with standard deviations of (12)

S(1)–C(1)–N(2)–C(3)	−8.0(7)
C(11)–C(1)–N(2)–C(3)	174.9(5)
S(1)–C(1)–C(11)–C(12)	14.4(7)
S(1)–C(1)–C(11)–C(16)	−166.5(4)
N(2)–C(1)–C(11)–C(12)	−168.3(5)
N(2)–C(1)–C(11)–C(16)	10.8(7)
C(1)–N(2)–C(3)–N(4)	173.0(5)
N(2)–C(3)–N(4)–C(41)	0.3(8)
N(2)–C(3)–N(4)–C(42)	177.6(5)
C(1)–C(11)–C(12)–C(13)	−179.1(5)
C(16)–C(11)–C(12)–C(13)	1.7(8)
C(1)–C(11)–C(16)–C(15)	178.2(5)
C(12)–C(11)–C(16)–C(15)	−2.7(8)
C(11)–C(12)–C(13)–C(14)	−0.8(10)
C(12)–C(13)–C(14)–C(15)	0.8(10)
C(13)–C(14)–C(15)–C(16)	−1.6(10)
C(14)–C(15)–C(16)–C(11)	2.7(10)

Table 8. Fractional co-ordinates of atoms with standard deviations of (12)

Atom	x	y	z
S(1)	0.402 3(3)	0.598 11(9)	0.332 84(25)
C(1)	0.136 3(8)	0.594 17(24)	0.202 7(6)
N(2)	−0.004 7(7)	0.546 88(20)	0.192 7(5)
C(3)	0.073 5(9)	0.496 41(24)	0.275 1(7)
N(4)	−0.059 2(7)	0.450 71(20)	0.285 4(5)
C(41)	−0.301 2(10)	0.454 8(3)	0.203 1(10)
C(42)	0.027 1(11)	0.392 83(24)	0.371 9(8)
C(11)	0.034 7(9)	0.646 61(23)	0.092 6(6)
C(12)	0.164 6(10)	0.695 23(24)	0.061 5(7)
C(13)	0.066 0(12)	0.743 9(3)	−0.039 5(8)
C(14)	−0.162 2(13)	0.746 8(3)	−0.115 8(8)
C(15)	−0.290 4(11)	0.698 9(3)	−0.085 6(8)
C(16)	−0.196 9(10)	0.649 3(3)	0.012 4(7)

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