Heterocyclic Analogues of Cyclopentadienylidenecycloheptatriene derived from 1,3,4-Oxadiazole and 1,2,4-Triazole

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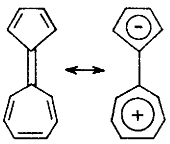
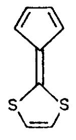
Heterocyclic systems having the same π-electron configuration as cyclopentadienylidenecycloheptatriene are of two types, covalent and dipolar. The stable covalent 2-fluoren-9-ylidene-3,5-dimethyl-Δ^4-1,3,4-oxadiazoline (10) and 5-fluoren-9-ylidene-1,3,4-trimethyl-Δ^2-1,2,4-triazoline (15) have been prepared starting with fluorene-9-carbohydrazide. The synthesis of the unstable dipolar anhydro-5-fluoren-9-yl-2,3-diphenyl-1,3,4-oxadiazolium hydroxide (20) and attempts to obtain its 5-diphenylmethyl analogue are described.

Numerous heterocyclic compounds, iso-π-electronic with cyclopentadienylidenecycloheptatriene ('sesquifulvalene') (1), are known in which pairs of carbon atoms linked by double bonds as in formula (1*a*) are replaced by heteroatoms capable of contributing two π-electrons. The simplest are the dihydropyridines discussed in the preceding paper; more elaborate structures are exemplified by the dithiafulvalene (2)[1a] and derivatives of the aza-compounds (3)[1a] and (4)[1b] which contain, in addition to the 2π-heteroatoms, nitrogen atoms each contributing one π-electron, in place of single carbon atoms. All these covalent compounds can be represented by classical formulae without formal charges. A different type of sesquifulvalene analogue can be envisaged for which no uncharged structure can be written. Such molecules are constructed by replacing a pair of carbon atoms joined by a single bond in formula (1*a*) by a heteroatom with a lone pair of electrons, giving rise, for example, to the hypothetical pyridinium ylide (5), the parent of the dipolar series. A compound of this type has now been prepared.

We recently found[2] that diacylhydrazines on treatment with acetic anhydride and perchloric acid yield 1,3,4-oxadiazolium salts which in turn are transformed into 1,2,4-triazolium salts by the action of primary amines.[3] On applying these reactions to fluorene-9-carbohydrazides we obtained a number of fluorenyl-oxadiazolium and -triazolium salts which were converted into heterocyclic analogues of sesquifulvalene by proton abstraction.

Treatment of fluorene-9-carbohydrazide with acetic anhydride and perchloric acid gave a salt which yielded the fluorenyl(methyl)oxadiazole (6) on basification. Methylation of this oxadiazole yielded a single quaternary salt isolated as the perchlorate; triethyloxonium fluoroborate produced an analogous salt. It was of crucial importance to determine which nitrogen atom had been alkylated, since the site of quaternisation governs the covalent or dipolar character of the derived anhydro-bases. The n.m.r. spectra (see Table) of trifluoroacetic acid solutions of both salts exhibited *C*-methyl singlets at τ 7·1 indicating that the methyl groups are attached to C-5 of the oxadiazolium ring; protons of C-5 methyl groups resonate[2] at τ 7·1—7·2, those of the less shielded C-2 methyl groups at 6·9.† Hence methylation and ethylation had occurred at N-3, giving the salts (7) and (8), respectively. The n.m.r. spectrum of a solution of the salt (6) in trifluoroacetic acid exhibited a single methyl resonance at τ 7·24; hence protonation also takes place solely at N-3. Alkylation at the more hindered nitrogen atom was unexpected; however, since protonation occurs at the same position it appears that the reactions are governed by electronic rather than steric effects and their course is determined by the greater inductive electron release of the secondary carbon atom attached to C-2 than that of the methyl group at C-5.


(1a) (1b)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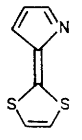
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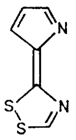
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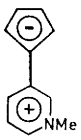
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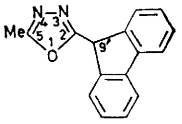
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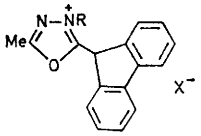
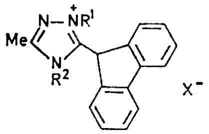

(7) R = Me, X = ClO_4
(8) R = Et, X = BF_4
(9) R = H, X = $CF_3 \cdot CO_2$


(11) R^1 = Me, R^2 = Ph, X = ClO_4
(13) R^1 = Et, R^2 = Ph, X = BF_4
(14) R^1 = Et, R^2 = Me, X = BF_4

Treatment of the *N*-methyl salt (7) with triethylamine gave the bright yellow covalent sesquifulvalene analogue (10) which was reconverted into the salt by perchloric acid. The structure of the base is confirmed by the

† We have since examined numerous further 2- and 5-methyl-substituted oxidiazolium salts and have not found an exception to this generalisation (unpublished work with S. R. Dando).

[1] (*a*) R. Gompper, cited in A. Lüttringhaus, H. Berger, and H. Prinzbach, *Tetrahedron Letters*, 1965, 2121; (*b*) R. Gompper and R. Weiss, *Angew. Chem.*, 1968, **80**, 277.

[2] G. V. Boyd, *Chem. Comm.*, 1967, 954.

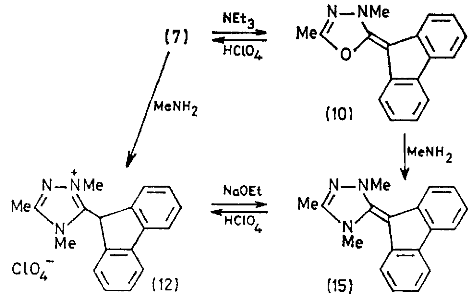
[3] G. V. Boyd and A. J. H. Summers, *Chem. Comm.*, 1968, **549**.

n.m.r. spectrum, which lacked the methine proton signals shown by compounds (6)—(9) but contained two methyl singlets. Compound (10) represents a highly substituted anhydro-base. Its stability is therefore not surprising and provides further evidence for the constitution of the parent oxadiazolium salt. We were unable to convert the salt (7) into the *N*-phenyltriazolium salt (11) by the action of aniline in boiling acetic acid; treatment with ethanolic methylamine, however, readily yielded the analogous *N*-methyltriazolium perchlorate (12). The *N*-ethyloxadiazolium fluoroborate (8) gave the triazolium salts (13) and (14) by reaction with aniline and methylamine, respectively. Deprotonation of the perchlorate (12) with sodium ethoxide afforded the stable yellow anhydro-base (15) whose electronic spectrum [$\lambda_{max.}$(MeCN) 357 and 420 nm.] closely resembled that of its oxygen analogue (10), and which could be re-protonated to the salt (12). The triazoline was also formed by the action of methylamine on compound (10), a reaction analogous to the formation of *N*-alkylpyridones from pyrones and alkylamines and indicative of the polar character of the oxadiazoline anhydro-base.

^{1}H n.m.r. spectra (τ values)

Compound	Benzene protons	H-9′	CMe	*N*-alkyl
(6) [a]	2·15—2·80(m)	4·57(s)	7·65(s)	
(6) [b] [= (9)]	2·15—2·70(m)	4·62(s)	7·24(s)	
(7) [b]	2·15—2·70(m)	4·63(s)	7·10(s)	5·93(s, Me)
(8) [b]	2·17—2·70(m)	4·60(s)	7·09(s)	5·61(q) and 8·38(t) (Et)
(12) [b,c]	2·10—2·68(m)	4·49(s)	7·37(s)	5·83(s, 1-Me), 7·23(s, 4-Me)
(13) [b]	2·20—2·72(m)	4·50(s)	7·63(s)	5·48(q) and 8·42(t) (Et)
(14) [b]	2·05—2·70(m)	4·45(s)	7·36(s)	7·23(s, Me), 5·52(q), and 8·30(t) (Et)
(15) [d,e]	2·10—2·85(m)			6·94(s, Me), 7·00(s, Me), and 7·93(s, Me)
(19) [b]	2·18—2·72(m)	4·43(s)		
(23) [b]	2·20—2·80(m)	3·99(s)		
(26) [b]	2·50—2·75(m)	4·35(s)		

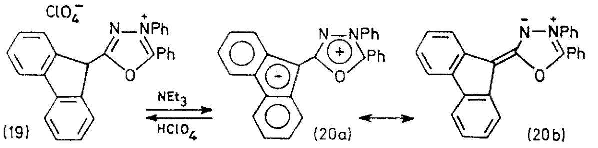
[a] In $CDCl_3$. [b] In $CF_3{\cdot}CO_2H$. [c] The assignment of the three methyl signals is based on a comparison with the spectra of the salts (13) and (14). [d] In $(CD_3)_2SO$. [e] The spectrum of the base (10) could not be determined because of the low solubility of the compound.

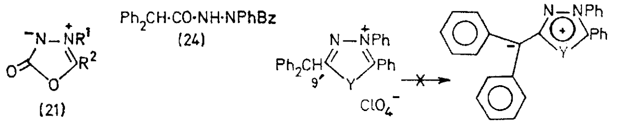


N′-Phenylfluorene-9-carbohydrazide (16) was the starting material for the preparation of a fluorenyloxadiazolium salt quaternised on the other nitrogen atom, a prerequisite for conversion into a dipolar anhydro-base. This hydrazide did not yield the expected methyl-substituted oxadiazolium perchlorate on treatment with acetic anhydride–perchloric acid, nor could its 1-formyl derivative (17) be cyclised; the benzoyl derivative (18), however, afforded the diphenyloxadiazolium perchlorate (19) of unambiguous structure. When this salt was treated with triethylamine a purple solid [$\lambda_{max.}$(MeCN) 536 nm.] was obtained which was stable towards water, light, and air but rapidly decomposed in all solvents and on warming and could therefore not be purified for analysis. However, it could be reconverted into the salt (19) and this, together with the i.r. spectrum which showed the absence of NH and amide groups, is consistent with the dipolar structure (20), which was confirmed by the mass spectrum [*m*/*e* 386 (M^+), 105 ($PhCO^+$, PhN_2^+), 77 (Ph^+), and 51 ($C_4H_3^+$); this fragmentation pattern closely resembles that proposed[4] for 2,5-diphenyl-1,3,4-oxadiazole].

$C_{13}H_9CO{\cdot}NH{\cdot}NPhR$

(16) R = H
(17) R = CHO
(18) R = Bz





(23) Y = O
(26) Y = NPh

(22) Y = O
(25) Y = NPh

We suggest that the dipolar sesquifulvalene analogue is stabilised by contribution from canonical forms such as (20*b*), which shows the relationship of this compound to the ‘ isomeric sydnones ’ (21).[5] The anhydro-base is, in fact, a mesoionic compound in which the exocyclic atom bearing part of the negative charge is carbon as in Grashey and Baumann's recently reported cyanomethylene analogues of mesoionic 1,2,4-triazolinones.[6] The importance of the contribution from the sesquifulvalenoid form (20*a*) in stabilising the mesoionic

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[4] J. L. Cotter, *J. Chem. Soc.*, 1964, 5491.

[5] M. Hashimoto and M. Ohta, *Bull. Chem. Soc. Japan*, 1961, **34**, 668; C. Ainsworth, *Canad. J. Chem.*, 1965, **43**, 1607.

[6] R. Grashey and M. Baumann, *Angew. Chem.*, 1969, **81**, 115.

molecule is indicated by our failure to isolate the closely related diphenylmethyl compound (22), which has all the structural features of the base (20) but for the absence of the cyclopentadiene ring. The precursor, the oxadiazolium salt (23), was readily prepared from the phenylhydrazide (24). Treatment of the salt with triethylamine under the same conditions as those which led to the formation of compound (20) resulted in an orange-red solution which soon faded in colour and deposited the original hydrazide (24). It appeared from the transient colour that the base (22) had been produced but was rapidly hydrolysed by traces of moisture. Repetition of the experiment with carefully dried reagents gave brown amorphous material. Similarly, the nitrogen analogue (25) could not be isolated when deprotonation of the corresponding triazolium perchlorate (26) was attempted.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra refer to Nujol mulls. Perchloric acid was of 70% strength.

2-*Fluoren*-9-*yl*-5-*methyl*-1,3,4-*oxadiazole* (6).—A cooled suspension of fluorene-9-carbohydrazide [7] (3·0 g.) in acetic anhydride (18 ml.) was treated with perchloric acid (2·5 ml.) at such a rate that the temperature did not rise above 40° and the resulting clear solution was set aside for 4 hr. Addition of ether precipitated the oily perchlorate (9; $X = ClO_4^-$) which was washed with ether and triturated with 5% sodium carbonate giving the *oxadiazole* (2·3 g., 70%), m.p. 147—148° (from ethanol), $\nu_{max.}$ 1590 and 1552 cm.$^{-1}$ (Found: C, 77·25; H, 4·7; N, 11·4. $C_{16}H_{12}N_2O$ requires C, 77·4; H, 4·85; N, 11·3%).

Quaternary Salts.—A solution of the foregoing oxadiazole (2·4 g.) and dimethyl sulphate (2·0 g.) in benzene (40 ml.) was refluxed overnight; the precipitated oil was washed with ether and dissolved in acetic acid (5 ml.) containing perchloric acid (1·4 ml.). Ether precipitated 2-*fluoren*-9-*yl*-3,5-*dimethyl*-1,3,4-*oxadiazolium perchlorate* (7) (2·5 g., 71%) as needles (from acetic acid), m.p. 187—189°, $\nu_{max.}$ 1640, 1610, 1598, and 1095 cm.$^{-1}$ (Found: C, 56·2; H, 4·15; N, 7·7. $C_{17}H_{15}ClN_2O_5$ requires C, 56·25; H, 4·15; N, 7·7%). A solution of the same oxadiazole (0·4 g.) in chloroform (35 ml.) was mixed with a 20% solution of triethyloxonium fluoroborate in dichloromethane (5 ml.). After 3 days the mixture was filtered from a precipitate (0·25 g.) and treated with ether; 3-*ethyl*-2-*fluoren*-9-*yl*-5-*methyl*-1,3,4-*oxadiazolium tetrafluoroborate* (8) separated (0·26 g., 44·5%), needles (from acetic acid), m.p. 158—160°, $\nu_{max.}$ 1620, 1599, and 1060 cm.$^{-1}$ (Found: C, 59·1; H, 4·6; N, 7·5. $C_{18}H_{17}BF_4N_2O$ requires C, 59·35; H, 4·7; N, 7·7%).

1,2,4-*Triazolium Salts*.—A suspension of the *N*-methyloxadiazolium perchlorate (7) (1·0 g.) in ethanol (3 ml.) was treated with 33% ethanolic methylamine solution (1·5 ml.); the mixture became warm, the solid dissolved, and 5-*fluoren*-9-*yl*-1,3,4-*trimethyl*-1,2,4-*triazolium perchlorate* (12) began to crystallise after a few seconds. It was collected next morning (0·8 g., 77%), needles (from acetic acid), m.p. 226—228°, $\nu_{max.}$ 1595, 1570, and 1095 cm.$^{-1}$ (Found: C, 57·45; H, 4·65; N, 11·15. $C_{18}H_{18}ClN_3O_4$ requires C, 57·55; H, 4·85; N, 11·2%). The *N*-ethyloxadiazolium fluoroborate (8) (0·2 g.) similarly gave 1-*ethyl*-5-*fluoren*-9-*yl*-3,4-*dimethyl*-1,2,4-*triazolium tetrafluoroborate* (14) (0·15 g., 72%), m.p. 217—219° (from acetic acid), $\nu_{max.}$ 1600, 1580, and 1050 cm.$^{-1}$ (Found: C, 60·55; H, 5·15; N, 11·2. $C_{19}H_{20}BF_4N_3$ requires C, 60·5; H, 5·35; N, 11·15%). 1-*Ethyl*-5-*fluoren*-9-*yl*-3-*methyl*-4-*phenyl*-1,2,4-*triazolium tetrafluoroborate* (13), m.p. 186—187° (from acetic acid–ether), $\nu_{max.}$ 1605, 1582, 1560, and 1060 cm.$^{-1}$ (Found: C, 65·9; H, 4·95; N, 9·5. $C_{24}H_{22}BF_4N_3$ requires C, 65·6; H, 5·05; N, 9·55%) was obtained (23%) when a mixture of the oxadiazolium fluoroborate (8) (0·36 g.), aniline (0·2 g.), and acetic acid (2 ml.) was boiled for 2 hr. and the cooled solution was treated with ether.

2-*Fluoren*-9-*ylidene*-3,5-*dimethyl*-Δ^4-1,3,4-*oxadiazoline* (10).—Addition of triethylamine (0·3 g.) to a solution of the dimethyloxadiazolium perchlorate (7) (0·76 g.) in acetonitrile (2 ml.) precipitated the yellow crystalline *anhydro-base* in quantitative yield (0·55 g.), needles (from acetonitrile), m.p. 175—176·5°, $\nu_{max.}$ 1654 and 1591 cm.$^{-1}$ (Found: C, 77·75; H, 5·25; N, 10·55. $C_{17}H_{14}N_2O$ requires C, 77·85; H, 5·4; N, 10·7%). Treatment of the base with perchloric acid regenerated the salt (7) (mixed m.p. and i.r. spectrum).

5-*Fluoren*-9-*ylidene*-1,3,4-*trimethyl*-Δ^2-1,2,4-*triazoline* (15).—(*a*) The oxadiazoline (10) (0·26 g.) was shaken with 33% ethanolic methylamine solution (5 ml.) for 5 hr. and then set aside for 2 days. The yellow *triazoline* (0·26 g., 94·5%) crystallised as needles (from acetonitrile), m.p. 255—257°, $\nu_{max.}$ 1600 cm.$^{-1}$ (Found: C, 78·15; H, 6·45; N, 15·55. $C_{18}H_{17}N_3$ requires C, 78·5; H, 6·25; N, 15·25%).

(*b*) The triazoline (0·36 g., 98%) was obtained by adding the triazolium perchlorate (12) (0·5 g.) to a solution prepared from sodium (0·2 g.) and ethanol (5 ml.). This sample was identical (m.p., mixed m.p., and i.r. spectrum) with that prepared in (*a*). Treatment with a solution of perchloric acid in acetic acid regenerated the salt (12).

N′-*Phenylfluorene*-9-*carbohydrazide* (16).—The published [8] procedure for the preparation of fluorene-9-carbonyl chloride from the acid and thionyl chloride gave unsatisfactory results in our hands; we therefore prepared the chloride by heating an intimate mixture of fluorene-9-carboxylic acid (20·0 g.) and phosphorus pentachloride (30·0 g.) at 70° for 1 hr. The mixture was then extracted repeatedly with light petroleum (b.p. 60—80°), the combined extracts on concentration deposited the acid chloride as colourless needles (20·0 g., 92%), m.p. 73—74° (lit.,[8] 77°). The chloride (10·0 g.) was added to an ice-cold solution of phenylhydrazine (6·2 g.) in pyridine (70 ml.). The mixture was kept overnight and then poured into 5N-hydrochloric acid (200 ml.). The precipitated *phenylhydrazide* (11·0 g., 84%) crystallised from ethanol as pale yellow needles, m.p. 213—214°, $\nu_{max.}$ 3320, 3260, 1640, and 1600 cm.$^{-1}$ (Found: C, 79·7; H, 5·3; N, 9·35. $C_{20}H_{16}N_2O$ requires C, 80·0; H, 5·35; N, 9·35%).

N′-*Acyl Derivatives of* N′-*Phenylfluorene*-9-*carbohydrazide*.—A mixture of the phenylhydrazide (16) (1·0 g.) and formic acid (5 ml.) was refluxed for 12 hr., cooled, and poured into ice-water. The precipitated 1-*formyl derivative* (17) (0·94 g., 86%) had m.p. 213° (decomp.) (from ethanol), $\nu_{max.}$ 3210, 1710, 1665, and 1595 cm.$^{-1}$ (Found: C, 76·7; H, 4·95; N, 8·25. $C_{21}H_{16}N_2O_2$ requires C, 76·8; H, 4·9; N, 8·55%). A mixture of the phenylhydrazide (16) (6·6 g.), benzoyl chloride (4·2 g.), and benzene (160 ml.) was heated under reflux until evolution of hydrogen chloride ceased

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[7] R. Stollé, H. Münzel, and F. Wolf, *Ber.*, 1913, **46**, 2339.

[8] R. Stollé and F. Wolf, *Ber.*, 1913, **46**, 2248.

(*ca.* 16 hr.). The resulting 1-*benzoyl derivative* (18) was recrystallised from acetone–ethanol (4·76 g., 53·5%); m.p. 236—237°, $\nu_{max.}$ 3300, 1709, 1655, and 1595 cm.$^{-1}$ (Found: C, 79·2; H, 4·95; N, 6·5. $C_{27}H_{20}N_2O_2$ requires C, 80·15; H, 5·0; N, 6·9%).

5-*Fluoren*-9-*yl*-2,3-*diphenyl*-1,3,4-*oxadiazolium Perchlorate and its Deprotonation*.—A suspension of the benzoyl derivative (18) (1·75 g.) in acetic anhydride (12 ml.) was treated with perchloric acid (1·5 ml.). The *oxadiazolium salt* was collected after 4 hr. and crystallised from acetic acid as colourless needles (1·3 g., 61%), m.p. 213° (decomp.), $\nu_{max.}$ 1610, 1600, and 1095 cm.$^{-1}$ (Found: C, 66·6; H, 3·95; N, 5·65. $C_{27}H_{19}ClN_2O_5$ requires C, 66·6; H, 3·95; N, 5·75%). Addition of triethylamine (0·5 ml.) to a solution of this salt (0·5 g.) in acetonitrile (1 ml.) caused precipitation of the purple 5-*fluoren*-9-*yl*-2,3-*diphenyl*-1,3,4-*oxadiazolium hydroxide anhydro*-(20) (0·4 g., 100%), m.p. 105—107° (decomp. with prior darkening and sintering), $\nu_{max.}$ 1612, 1600, and 1580 cm.$^{-1}$. When the base was added to a mixture of acetic acid and perchloric acid its colour was discharged and the perchlorate (19) was formed, identified by m.p., mixed m.p., and i.r. spectrum.

1-*Benzoyl*-2-*diphenylacetyl*-1-*phenylhydrazine* (24) was obtained by refluxing a mixture of 1-diphenylacetyl-2-phenylhydrazine [9] (15·1 g.), benzoyl chloride (7·03 g.), and benzene (200 ml.) overnight and collecting the product (19·7 g., 100%), which gave needles (from 1 : 1 acetone–ethanol or acetonitrile), m.p. 190—191·5° (resolidifies and then melts again at 206—207°), $\nu_{max.}$ 3200, 1690, and 1665 cm.$^{-1}$ (Found: C, 79·55; H, 5·3; N, 6·75. $C_{27}H_{22}N_2O_2$ requires C, 79·75; H, 5·45; N, 6·9%). Treatment of this hydrazide (3·5 g.) with acetic anhydride (28 ml.) followed by perchloric acid (3 ml.) gave an oil which slowly solidified. Recrystallisation from acetic acid afforded 5-*diphenylmethyl*-2,3-*diphenyl*-1,3,4-*oxadiazolium perchlorate* (23) (1·69 g., 40%), m.p. 124—126°, $\nu_{max.}$ 1600, 1560, and 1090 cm.$^{-1}$ (Found: C, 65·45; H, 4·25; N, 6·1. $C_{27}H_{21}ClN_2O_5$ requires C, 66·3; H, 4·35; N, 5·75%). This salt is rather unstable and easily hydrolysed to the hydrazide (24). A solution of the salt (1·0 g.) and aniline (0·38 g.) in acetic acid (5 ml.) was heated under reflux for 15 min., cooled, and treated with ether to incipient cloudiness. When cooled to −20° the mixture deposited crystals which showed amide bands in the i.r. spectrum. On boiling this salt in acetic acid for 10 min. 3-*diphenylmethyl*-1,4,5-*triphenyl*-1,2,4-*triazolium perchlorate* (26) was produced (0·6 g., 52%), m.p. 258—260°, $\nu_{max.}$ 1600, 1590, 1550, and 1095 cm.$^{-1}$ (Found: C, 70·05; H, 4·5; N, 7·3. $C_{33}H_{26}ClN_3O_4$ requires C, 70·25; H, 4·65; N, 7·45%). A solution of the oxadiazolium salt (23) (0·5 g.) in acetonitrile (5 ml.) on treatment with triethylamine (0·5 g.) turned orange-red and then brown and a colourless solid (0·2 g.) slowly separated which proved to be the phenylhydrazide (24). When the experiment was repeated with freshly dried reagents, and the brown solution was evaporated to dryness under reduced pressure, a dark intractable residue remained. Attempted deprotonation of the triazolium salt (26) with ethanolic sodium ethoxide gave unidentified colourless material exhibiting NH (3220) and amide (1680 and 1640 cm.$^{-1}$) bands in its i.r. spectrum; this was evidently not the ylide (25).

We thank the S.R.C. for a studentship (to M. D. H.).

[9/1521 *Received, September 5th*, 1969]

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[9] J. Staňek, *Chem. listy*, 1943, **37**, 161.