The Reaction of 1,2,3-Thiadiazoles and 1,2,3-Selenadiazoles with Nonacarbonyldi-iron [1]

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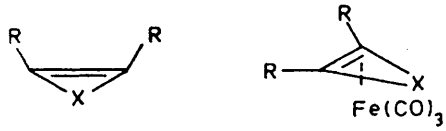
Carbene complexes [μ-(thiophenacylidene)-bis(tricarbonyliron) (*Fe–Fe*) derivatives (9) and the seleno-analogues (10)] are obtained by the reaction of phenyl-substituted 1,2,3-thiadiazoles and 1,2,3-selenadiazoles with nonacarbonyldi-iron. When the substituents at positions 4 and 5 of the thiadiazoles and selenadiazoles are different, two isomeric carbene complexes are produced, the minor isomer in each case being a rearrangement product. Evidence is presented that this rearrangement occurs before the carbene complexes are formed, and may involve antiaromatic thiirens and selenirens as the symmetrical intermediates.

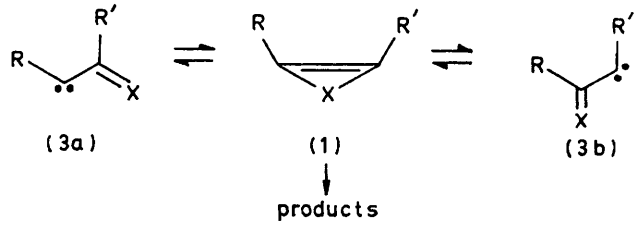
HETEROCYCLIC systems of the general structure (1), where X is an atom with a lone electron pair, are known only as reaction intermediates.† Their apparent instability can be attributed to their antiaromatic character, in that with four electrons contributed by the double bond and the lone pair, the ring systems are isoelectronic with cyclobutadiene. This paper describes attempts to stabilise such ring systems (where X = S or Se), as tricarbonyliron complexes (2), analogous to those formed by cyclobutadiene derivatives.



(1) (2)

Orgel has suggested that the stabilisation of cyclopropenyl derivatives by formation of metal complexes is likely to be less than in the case of cyclobutadiene, because of the decreased efficiency of the overlap between the occupied orbitals on the metal and the unfilled orbitals of the ligand.[4] Sulphur and selenium were chosen as the heteroatoms in the potential three-membered ring complexes with the intention of increasing the possibility of back donation from the metal. In the event, this has proved to be insufficient to permit the isolation of the complexes (2), although complexes of a different type have been obtained, and there is evidence to suggest that complexes of structure (2) may be reaction intermediates.

By analogy with the preparation of cyclobutadiene complexes, the most direct route to complexes of structure (2) appears to be dehalogenation of the 2,3-dichloro- or -dibromo-heterocyclic systems with nonacarbonyldi-iron. Experiments with 2,3-dichloroaziridines [5] have shown that this method is unsuccessful for the preparation of 1*H*-azirine complexes, however, and it was not applied to 2,3-dichlorothiirans or 2,3-dichloroselenirans because such compounds are unknown, except as unstable intermediates.[6] Instead, a route was chosen which was expected to give the carbene derivatives (3): if isomeric precursors are used, this method permits the detection of a 'symmetrical' intermediate such as the cyclic system (1) by the isolation of common products derived from the carbenes (3a and b) (Scheme).



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This technique has been used to identify oxirens (1; X = O) as intermediates in the photolysis of diazoketones,[7] and 1*H*-azirines (1; X = NR) in the pyrolysis of 1,2,3-triazoles.[8] The analogous carbene precursors where X = S or Se are 1,2,3-thiadiazoles (4) and 1,2,3-selenadiazoles (5). 1,2,3-Thiadiazoles have been shown to lose nitrogen on photolysis in solution, and thiocarbonylcarbenes have been suggested as intermediates [9] (although photolysis at low temperature in a solid matrix involves radical decomposition).[10] The photolysis of 5-methyl-1,2,3-thiadiazole has been claimed to involve a thiiren intermediate.[11] 1,2,3-Selenadiazoles have been shown to decompose thermally to give acetylenes, selenium, and nitrogen, the reaction being a useful synthetic route to acetylenes,[12a,b] but no studies of its mechanism have been reported. Photolysis of selenadiazoles appears to involve selenoketens as intermediates.[12c]

† For examples see refs. 2 and 3. An apparent exception is the thiiren oxide system, a derivative of which has been isolated; [3] in this system, however, the lone pair on the heteroatom is possibly in an orbital orthogonal to the π-bond.

[1] Preliminary communication, P. G. Mente and C. W. Rees, *J.C.S. Chem. Comm.*, 1972, 418.
[2] L. A. Carpino, L. V. McAdams, R. H. Rynbrandt, and J. W. Spiewak, *J. Amer. Chem. Soc.*, 1971, **93**, 476.
[3] L. A. Carpino and H.-W. Chen, *J. Amer. Chem. Soc.*, 1971, **93**, 785.
[4] L. E. Orgel, 'An Introduction to Transition-Metal Chemistry: Ligand-Field Theory,' Methuen, London, 1960, p. 154.
[5] D. J. Anderson, Ph.D. Thesis, University of Leicester, 1969.
[6] T. J. Barton and R. G. Zika, *J. Org. Chem.*, 1970, **35**, 1729.
[7] D. E. Thornton, R. K. Gosavi, and O. P. Strausz, *J. Amer. Chem. Soc.*, 1970, **92**, 1768; G. Frater and O. P. Strausz, *ibid.*, p. 6654.
[8] T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *Chem. Comm.*, 1971, 1519.
[9] W. Kirmse and L. Horner, *Annalen*, 1958, **614**, 4; K.-P. Zeller, H. Meier, and E. Müller, *Tetrahedron Letters*, 1971, 537.
[10] P. Krauss, K.-P. Zeller, H. Meier, and E. Müller, *Tetrahedron*, 1971, **27**, 5953.
[11] O. P. Strausz, J. Font, E. L. Dedio, P. Kebarle, and H. E. Gunning, *J. Amer. Chem. Soc.*, 1967, **89**, 4805.
[12] (*a*) I. Lalezari, A. Shafiee, and M. Yalpani, *Angew. Chem. Internat. Edn.*, 1970, **9**, 464; (*b*) *J. Org. Chem.*, 1971, **36**, 2836; (*c*) H. Meier and I. Menzel, *Tetrahedron Letters*, 1972, 445.

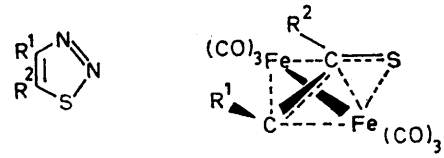
Other reactions in which thiirens may be involved include the addition of sulphur (generated by the flash photolysis of COS) to acetylene,[11] and the photolysis of the mesoionic 2,5-diphenyl-1,3-dithiol-4-one (6);[13] the isolation of diphenylacetylene from the latter reaction is interpreted as being a good indication that diphenylthiiren is an intermediate. Of these, the former method does not lend itself to trapping experiments with iron carbonyls; the reactions of compound (6) and related systems with transition metals are being investigated.[14]

Preparation of Thiadiazoles and Selenadiazoles.—The thiadiazoles (4) were prepared by a standard method, which involves the reaction of the appropriate ketone ethoxycarbonylhydrazones with thionyl chloride.[15] The derivatives (4b—e) are new compounds. They constitute two pairs of isomers, the t-butyl derivatives being chosen to provide an efficient marker in the n.m.r. spectra for the detection of any 'crossover' products. In the preparation of the thiadiazoles (4b and c) the reactions with thionyl chloride were slow, presumably because of steric retardation by the t-butyl groups. In each case an intermediate was isolated when the reaction was stopped after a short time. The intermediates, which are assigned structures (7a and b) on the basis of their analyses and spectra, could be converted into the corresponding thiadiazoles on further heating, and their presence provides a good indication that the mechanism of formation of the thiadiazoles proposed by Hurd and Mori[15] is correct.

The selenadiazoles (5) were prepared by the reactions of the appropriate ketone semicarbazones or ethoxycarbonylhydrazones with selenium dioxide.[12,16]

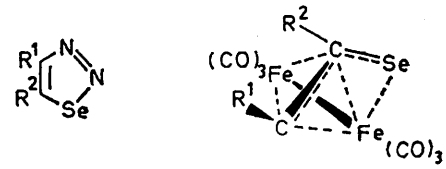
Reaction with Nonacarbonyldi-iron.—Nonacarbonyldi-iron has been shown to catalyse the elimination of nitrogen from organic azides.[17,18] Iron carbonyls form complexes with several heterocyclic systems containing the N=N linkage, some of these complexes being stable and isolable.[18,19] Thus it was reasonable to expect a reaction between nonacarbonyldi-iron and thiadiazoles, possibly resulting in a catalysed elimination of nitrogen *via* the open-chain diazo-thione tautomers of the thiadiazoles.

When 4,5-diphenyl-1,2,3-thiadiazole (4a) was stirred with an excess of nonacarbonyldi-iron in dry 1,2-dimethoxyethane at room temperature for 12 h, there was some evidence of complex formation, in that the solution became coloured, but the complex did not survive an attempted chromatographic separation. The reaction was then carried out under reflux (82°) for 20 h. T.l.c. showed an orange product, and an orange-brown oil was isolated by preparative layer chromatography. On crystallisation at low temperature this gave a red crystalline complex, the physical properties of which are identical to those reported[20] for a complex obtained by the irradiation of the nickel derivative (8) in the presence of pentacarbonyliron. An *X*-ray diffraction study has



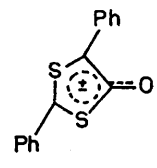
(4) (9)

a; $R^1 = R^2 = Ph$
b; $R^1 = Bu^t, R^2 = Ph$
c; $R^1 = Ph, R^2 = Bu^t$
d; $R^1 = p\text{-}Bu^tC_6H_4, R^2 = Ph$
e; $R^1 = Ph, R^2 = p\text{-}Bu^tC_6H_4$



(5) (10)

a; $R^1 = R^2 = Ph$
b; $R^1 = p\text{-}Bu^tC_6H_4, R^2 = Ph$
c; $R^1 = Ph, R^2 = p\text{-}Bu^tC_6H_4$



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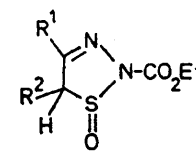
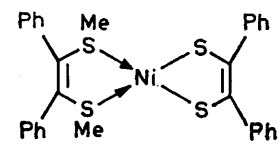


(7)

a; $R^1 = Bu^t, R^2 = Ph$
b; $R^1 = Ph, R^2 = Bu^t$



(8)

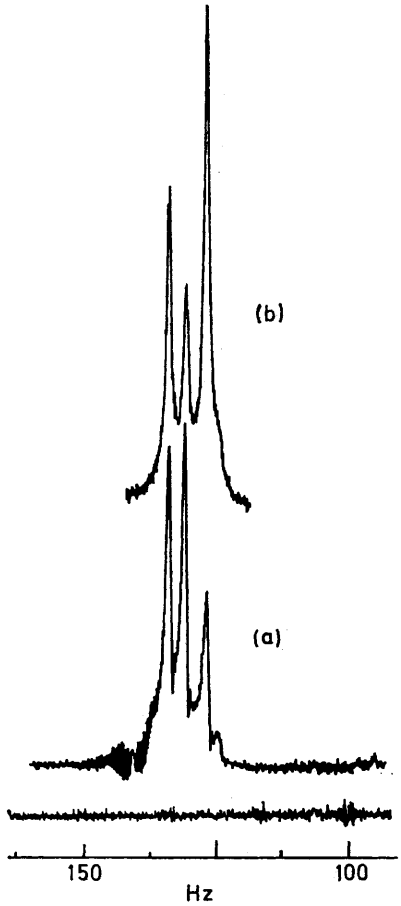
shown this complex to have the structure (9a), containing a phenyl(thiobenzoyl)carbene system.

Analogous complexes were obtained from the thiadiazoles (4b—e) and from the selenadiazoles (5a—c). The selenadiazoles reacted with nonacarbonyldi-iron much more rapidly than the corresponding thiadiazoles,

[13] H. Kato, M. Kawamura, T. Shiba, and M. Ohta, *Chem. Comm.*, 1970, 959.
[14] T. L. Gilchrist, G. Gymer, and C. W. Rees, *Abstr. Twenty-third Internat. Congr. Pure Appl. Chem.*, 1971, **2**, 275.
[15] C. D. Hurd and R. I. Mori, *J. Amer. Chem. Soc.*, 1955, **77**, 5359; R. Raap and R. G. Micetich, *Canad. J. Chem.*, 1968, **46**, 1057.
[16] I. Lalezari and A. Shafiee, *Tetrahedron Letters*, 1969, 5105.
[17] M. Dekker and G. R. Knox, *Chem. Comm.*, 1967, 1243.
[18] C. D. Campbell and C. W. Rees, *Chem. Comm.*, 1969, 537.
[19] R. P. Bennett, *Inorg. Chem.*, 1970, **9**, 2184.
[20] G. N. Schrauzer, H. N. Rabinowitz, J. A. K. Frank, and I. C. Paul, *J. Amer. Chem. Soc.*, 1970, **92**, 212.

the reactions being complete within a few min at 80°. The physical properties of all the complexes were similar, and consistent with the carbene structures (9b—e) and (10a—c).

In a second series of experiments, the crude complexes obtained from the chromatography plates were examined by n.m.r. spectroscopy before further purification. The spectra of the products obtained from the reaction of the thiadiazoles (4d and e) with nonacarbonyldi-iron each showed the same three peaks in the



^{1}H N.m.r. spectra (100 MHz; $CDCl_3$) of product mixtures from (a) 5-phenyl-4-*p*-t-butylphenyl-1,2,3-thiadiazole and (b) 4-phenyl-5-*p*-t-butylphenyl-1,2,3-thiadiazole with nonacarbonyldi-iron. Signals are from (left to right) 1-phenyl-2-*p*-t-butylphenylacetylene; complex (9d); complex (9e)

t-butyl region (see Figure), but in different proportions. The signals were assigned to the complexes (9d) and (9e) and to 1-phenyl-2-*p*-t-butylphenylacetylene by comparison with spectra of authentic specimens of these compounds, and by observing peak enhancement on addition of pure specimens of the products. The spectra show that in each of the two product mixtures the minor complex formed corresponds to a ' crossover ' product, in which the sulphur atom is no longer attached to the same carbon atom as in the starting thiadiazole. Thus partial, but not complete, scrambling of the two aryl groups has occurred.

Similar results were obtained with the reaction products from the thiadiazoles (4b and c) with nonacarbonyldi-iron, although the extent of crossover in these systems was much less. The crude product mixture from the thiadiazole (4b) showed two signals in the t-butyl region of the n.m.r. spectrum, which were assigned to the complexes (9b) and (9c); 3,3-dimethyl-1-phenylbut-1-yne was shown to be absent. The signal from the crossover product (9c) was only 14% of the intensity of that from complex (9b), however, indicating a much smaller proportion of rearrangement than in the earlier examples. In the case of the product from the thiadiazole (4c), only one signal was observed in this region of the n.m.r. spectrum, corresponding to the complex (9c). There was thus no evidence of equilibration in this system.

The results with the selenadiazoles (5b and c) closely paralleled those obtained from the corresponding thiadiazoles (4d and e). In each case three signals were obtained in the t-butyl region of the n.m.r. spectra, corresponding to those of the pure complexes (10b) and (10c) and that of 1-phenyl-2-*p*-t-butylphenylacetylene. The ratios of minor to major isomers in these and in the thiadiazole experiments are shown in the Table.

N.m.r. analysis of product mixtures

Starting material	Complexes identified	Ratio of minor to major isomer	
(4b)	(9b), (9c)	(9c) : (9b)	12 : 88
(4c)	(9c)	(9b) : (9c)	<5 : 95
(4d)	(9d), (9e)	(9e) : (9d)	31 : 69
(4e)	(9d), (9e)	(9d) : (9e)	28 : 72
(5b)	(10b), (10c)	(10c) : (10b)	24 : 76
(5c)	(10b), (10c)	(10b) : (10c)	25 : 75

Although the chromatographic analysis of the products from reactions with nonacarbonyldi-iron indicated that other products were formed, these were not investigated closely. A purple complex produced in the selenadiazole reactions was identified as the known [21] complex $Fe_3(CO)_9Se_2$; a similar purple product was observed from the thiadiazole reactions, and this was probably the analogous sulphur complex,[21] $Fe_3(CO)_9S_2$. Considerable amounts of the starting thiadiazoles or selenadiazoles could be recovered by solvent extraction of the lower region of the chromatography plates, although all the starting materials had appeared to be consumed: the most likely explanation is that unstable iron complexes of the thiadiazoles and selenadiazoles are formed, which then decompose on the chromatography plates to regenerate the heterocyclic precursors. Attempts to increase the yields of the carbene complexes by using more vigorous reaction conditions than those described were not successful.

Reaction Mechanisms.—The results of the n.m.r. studies indicate that the major product from the unsymmetrical thiadiazoles retains the C–C–S skeleton of the starting material, but that a minor product does not. Thus, equilibration has taken place, but it is incomplete. One possible explanation is that the formation of the products involves two competing reaction paths, of which the minor one proceeds through some species in

[21] W. Hieber and J. Gruber, *Z. anorg. Chem.*, 1958, **296**, 91.

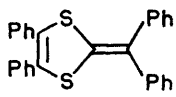
which both the carbon atoms of the thiadiazole skeleton become bonded to the sulphur atom in an equivalent fashion. Another explanation is that only the thiocarbonylcarbene complex with the original C–C–S skeleton is formed first, but that it then undergoes a slow equilibration on further heating, or in the presence of nonacarbonyldi-iron.

The latter possibility, that complexes such as (9d and e) can be interconverted under the reaction conditions, was tested experimentally.

Complex (9d) was unchanged after heating under reflux in tetrahydrofuran for 48 h. In a similar experiment with nonacarbonyldi-iron, complex (9d) was again recovered unchanged, and there was no evidence for the formation of the isomeric complex (9e). From these experiments it appears that the symmetrical species must be formed before these final products.

It has been shown that tetraphenyldithiafulvene (11) and tetraphenyldithiacyclohexadiene (12) are products of the photochemical decomposition of 4,5-diphenyl-1,2,3-thiadiazole.[9] The possibility that the complex (9a) was formed through (11) or (12) as intermediate was ruled out by subjecting these compounds to the reaction conditions: the complex (9a) was not formed. It was also shown that there was no interconversion of the isomeric thiadiazoles (4d and e) under the reaction conditions.

Thus, thiirens (1) or their iron complexes (2) remain as possible structures for the symmetrical intermediates involved in the reaction, although positive evidence for



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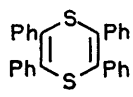

(12)

their involvement is lacking. From the point of view of using such complexes in organic synthesis, however, the fact that the ligands are bound to the metal in an open form in complexes (9) and (10) may not be important. The synthetic potential of the complexes, and the extension of the reaction to other diaza-heterocyclic compounds, are under investigation.

EXPERIMENTAL

Thiadiazoles.—*4,5-Diphenyl-1,2,3-thiadiazole* (4a). This was prepared (89%) by the reaction [15] of deoxybenzoin ethoxycarbonylhydrazone [22] with thionyl chloride, and had m.p. 93—94° (lit.,[23] 93—94°).

5-Phenyl-4-t-butyl-1,2,3-thiadiazole (4b). (*a*) Ethyl carbazate (6·0 g) and 3,3-dimethyl-1-phenylbutan-2-one [24] (6·0 g) were heated under reflux for 30 h in n-propanol (30 ml) containing a drop of hydrochloric acid. The solvent was removed and the residue recrystallised to give the *ethoxycarbonylhydrazone* (3·0 g, 27%), m.p. 106—108° (from aqueous ethanol) (Found: C, 69·0; H, 8·5; N, 10·8. $C_{15}H_{22}N_2O_2$ requires C, 68·7; H, 8·45; N, 10·7%).

(*b*) The ethoxycarbonylhydrazone (2·2 g) and thionyl chloride (3 ml) were heated under reflux for 11 h. The excess of thionyl chloride was distilled off and the residue recrystallised once from ether (with cooling to −80°) and twice from petroleum to give the *thiadiazole* (4b) (0·72 g, 39%), m.p. 67—69° (Found: C, 66·3; H, 6·6; N, 13·0; S, 14·7. $C_{12}H_{14}N_2S$ requires C, 66·0; H, 6·5; N, 12·8; S, 14·7%). If the reaction was stopped after a shorter period of reflux, an intermediate was isolated instead. Evaporation of the solution after reflux for 1 h gave *ethyl 2,5-dihydro-5-phenyl-4-t-butyl-1,2,3-thiadiazole-2-carboxylate S-oxide* (7a), m.p. 119·5—120·5° (from petroleum) (Found: C, 58·7; H, 6·6; N, 9·1; S, 10·5%; *m/e*, 308. $C_{15}H_{20}N_2O_3S$ requires C, 58·4; H, 6·5; N, 9·1; S, 10·4%; *M*, 308); $\nu_{max.}$ (Nujol) 1707 cm^{-1}.

4-Phenyl-5-t-butyl-1,2,3-thiadiazole (4c). (*a*) Ethyl carbazate (3·0 g), 3,3-dimethylbutyrophenone [24] (4·0 g), and n-propanol (20 ml) containing a crystal of iodine, were heated under reflux for 7 h. The solution was evaporated to dryness and the residue recrystallised to give the *ethoxycarbonylhydrazone* (77%), m.p. 120—122° (from propan-2-ol) (Found: C, 68·6; H, 8·7; N, 10·9. $C_{15}H_{22}N_2O_2$ requires C, 68·7; H, 8·45; N, 10·7%).

(*b*) The ethoxycarbonylhydrazone (1·2 g) and thionyl chloride (10 ml) were heated under reflux for 21 h and the excess of thionyl chloride was then distilled off. The residue was purified by chromatography [silica; petroleum–dichloromethane (1 : 1)], and was crystallised to give the *thiadiazole* (4c) (0·63 g, 63%), m.p. 98—100° (from hexane) (Found: C, 65·9; H, 6·3; N, 12·7; S, 14·6. $C_{12}H_{14}N_2S$ requires C, 66·0; H, 6·5; N, 12·8; S, 14·7%). Evaporation of the reaction mixture after reflux for 0·5 h gave *ethyl 2,5-dihydro-4-phenyl-5-t-butyl-1,2,3-thiadiazole-2-carboxylate S-oxide* (7b), m.p. 146° (from propan-2-ol) (Found: C, 58·3; H, 6·6%; *m/e*, 308. $C_{15}H_{20}N_2O_3S$ requires C, 58·4; H, 6·5%; *M*, 308).

5-Phenyl-4-p-t-butylphenyl-1,2,3-thiadiazole (4d). (*a*) Benzyl *p*-t-butylphenyl ketone [25] (20 g), ethyl carbazate (10·5 g), and n-propanol (80 ml) containing a crystal of iodine, were heated under reflux for 6·5 h. The solution was evaporated and the residue crystallised to give the *ethoxycarbonylhydrazone* (22 g, 82%), m.p. 132—133° (from propan-2-ol) (Found: C, 74·5; H, 7·7; N, 8·5. $C_{21}H_{26}N_2O_2$ requires C, 74·5; H, 7·7; N, 8·3%).

(*b*) The ethoxycarbonylhydrazone (10·0 g) and thionyl chloride (10 ml) were heated at 60° for 2 h. The excess of thionyl chloride was removed and the residue crystallised to give the *thiadiazole* (4d) (7·6 g, 87%), m.p. 117—118° (from methanol) (Found: C, 73·3; H, 6·0; N, 9·3; S, 11·0. $C_{18}H_{18}N_2S$ requires C, 73·4; H, 6·2; N, 9·5; S, 10·9%).

4-Phenyl-5-p-t-butylphenyl-1,2,3-thiadiazole (4e). (a) *Phenyl p-t-butylbenzyl ketone.* *p*-t-Butylphenylacetic acid (67·9 g) and phosphorus trichloride (24 g) were heated for 1 h at 100°. The acid chloride was extracted from the mixture with benzene (37 ml) and the extract was added dropwise to a mixture of aluminium chloride (55 g) in carbon disulphide (100 ml) at −20° during 2 h. The mixture was stirred at 0° for 10 h then poured on to ice-cold dilute hydrochloric acid. Extraction with dichloromethane followed by distillation through a spinning-band column gave the *ketone* (35 g, 39%), b.p. 175—176° at 2·5 mmHg, m.p. 59·5—60·5° (Found: C, 85·9; H, 7·9. $C_{18}H_{20}O$ requires C, 85·7; H, 8·0%).

[22] N. Rabjohn and H. D. Barnstorff, *J. Amer. Chem. Soc.*, 1953, **75**, 2259.
[23] H. Staudinger and J. Segwart, *Ber.*, 1916, **49**, 1918.
[24] H. O. House and E. J. Grubbs, *J. Amer. Chem. Soc.*, 1959, **81**, 4733.
[25] R. C. Fuson and L. I. Krimen, *J. Amer. Chem. Soc.*, 1955, **77**, 994.

(b) The ketone (22·0 g), ethyl carbazate (12 g), ethanol (50 ml), and a trace of toluene-*p*-sulphonic acid were heated under reflux for 5 h. The solution was cooled to −10° and the crystalline product was filtered off. Recrystallisation gave the *ethoxycarbonylhydrazone* (23·7 g, 80%), m.p. 134—136° (from methanol) (Found: C, 74·3; H, 7·55; N, 8·6%).

(c) The ethoxycarbonylhydrazone (6·0 g) and thionyl chloride (6 ml) were carefully mixed at −10°. Dry toluene (10 ml) was added and the solution heated at 60° for 0·5 h. The solvent was then removed and the oily residue dissolved in methanol. The product crystallised when the solution was cooled to 0°. Recrystallisation gave the *thiadiazole* (4e) (3·2 g, 61%), m.p. 111—112° (from methanol) (Found: C, 73·2; H, 6·2; N, 9·7; S, 10·8%).

Selenadiazoles.—*4,5-Diphenyl-1,2,3-selenadiazole* (5a). Deoxybenzoin semicarbazone (3·0 g), selenium dioxide (1·6 g; resublimed), and acetic acid (25 ml) were stirred at room temperature for 6 days. The mixture was then filtered and the filtrate evaporated under reduced pressure. The residue was crystallised to give the selenadiazole (5a) (2·0 g, 59%), m.p. 76—77° (from propan-2-ol) (lit.,[12a] 125° *) (Found: C, 59·1; H, 3·6; N, 10·0; *m/e*, 285. Calc. for $C_{14}H_{10}N_2Se$: C, 59·0; H, 3·5; N, 9·8%; *M*, 285). The selenadiazole gave diphenylacetylene (98%), m.p. 53—55°, when heated under reflux in n-propanol.

5-Phenyl-4-p-t-butylphenyl-1,2,3-selenadiazole (5b). (*a*) Benzyl *p*-t-butylphenyl ketone was converted into its *semicarbazone*, m.p. 163—167° (from petroleum–ethanol) (Found: C, 73·9; H, 7·4; N, 13·7. $C_{19}H_{23}N_3O$ requires C, 73·75; H, 7·5; N, 13·6%).

(*b*) The semicarbazone (3·1 g), selenium dioxide (1·5 g; resublimed), and acetic acid (50 ml) were stirred at room temperature for 7 days. The inorganic solids were filtered off and the filtrate evaporated under reduced pressure. The residue was crystallised to give the *selenadiazole* (5b) (2·9 g, 85%), m.p. 110—111° (from propan-2-ol) (Found: C, 63·4; H, 5·3; N, 8·2. $C_{18}H_{18}N_2Se$ requires C, 63·3; H, 5·3; N, 8·2%).

4-Phenyl-5-p-t-butylphenyl-1,2,3-selenadiazole (5c). Phenyl *p*-t-butylbenzyl ketone ethoxycarbonylhydrazone (3·4 g), selenium dioxide (1·5 g; resublimed), and acetic acid (15 ml) were stirred at room temperature for 7 days. The inorganic solids were filtered off, and the filtrate evaporated under reduced pressure. The residue was extracted with dichloromethane and the solution washed with aqueous sodium carbonate and water. Preparative layer chromatography [kieselgel; petroleum–dichloromethane (4 : 1)] gave the *selenadiazole* (1·5 g, 44%), m.p. 129·5—130·5° (from methanol) (Found: C, 63·7; H, 5·3; N, 8·5. $C_{18}H_{18}N_2Se$ requires C, 63·3; H, 5·3; N, 8·2%).

Acetylenes.—*3,3-Dimethyl-1-phenylbut-1-yne*. This was prepared [26] from phenylacetylene and t-butyl bromide and had b.p. 80—85° at 10 mmHg (lit.,[27] 84° at 10 mmHg); i.r. spectrum identical with that reported; [27] τ (100 MHz; $CDCl_3$) 8·68 (Bu^t).

1-Phenyl-2-p-t-butylphenylacetylene. 5-Phenyl-4-*p*-t-butylphenyl-1,2,3-selenadiazole (5b) (1·0 g) was heated under reflux in *p*-xylene for 20 h. The mixture was then evaporated to dryness and the residue purified by column chromatography (silica). Petroleum eluted the *acetylene* (0·50 g, 83%), m.p. 70—71° (from methanol); the crystals melted at 62° and re-solidified at 64° (Found: C, 92·2; H, 8·0. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%); τ (100 MHz; $CDCl_3$) 8·67 (Bu^t).

Reactions with Nonacarbonyldi-iron. General Procedure.—To the dry solvent (25 ml) was added the thiadiazole or selenadiazole (2 mmol). 1,2-Dimethoxyethane and tetrahydrofuran were both used as solvents in different runs and no differences were observed. The solution was heated to reflux and stirred under nitrogen [with the selenadiazoles longer periods (1—3 days) at room temperature were equally effective]; nonacarbonyldi-iron (0·7—1·5 g) was then added in portions at intervals during the reaction. The mixture was filtered and the filtrate evaporated under reduced pressure. The residue was subjected to plate chromatography (kieselgel; 100 × 25 × 0·1 cm) in petroleum. The organometallic complexes were isolated from orange bands on the developed plates by extraction with ether. The extracted material was then either examined directly by n.m.r. spectroscopy, or subjected to further chromatographic purification followed by crystallisation in order to obtain pure specimens of the major components.

4,5-Diphenyl-1,2,3-thiadiazole in dimethoxyethane for 24 h gave μ-[α-phenyl(thiophenacylidene]-bis(tricarbonyliron)(*Fe–Fe*) (9a) (14%), m.p. 125—127° (lit.,[12] 125—126°) (Found: C, 49·0; H, 2·0%; *m/e* 489·8896. Calc. for $C_{20}H_{10}Fe_2O_6S$: C, 49·0; H, 2·1%; *M*, 489·8896; $\nu_{max.}$ (cyclohexane) 2075s, 2039s, 2035, 2004s,sh, 1999s, 1990w, and 1985w cm^{-1} (C=O). An authentic specimen of this complex, prepared as in ref. 12, had an identical i.r. spectrum (cyclohexane).

5-Phenyl-4-t-butyl-1,2,3-thiadiazole (0·450 g) in dimethoxyethane for 48 h gave μ-[α-*t-butyl*(*thiophenacylidene*)]-*bis*(*tricarbonyliron*)(Fe–Fe) (9b) (0·051 g, 5%), m.p. 116—117° (from petroleum) (Found: C, 46·3; H, 3·3%; *m/e* 470. $C_{18}H_{14}Fe_2O_6S$ requires C, 46·0; H, 3·0%; *M*, 470); τ (100 MHz; $CDCl_3$) 8·88 (Bu^t).

4-Phenyl-5-t-butyl-1,2,3-thiadiazole (0·500 g) in dimethoxyethane for 48 h gave μ-(3,3-*dimethyl*-1-*phenyl*-2-*thioxobutylidene*)-*bis*(*tricarbonyliron*)(Fe–Fe) (9c) (0·061 g, 6%), m.p. 74·5—75·5° (from petroleum) (Found: C, 46·1; H, 3·15. $C_{18}H_{14}Fe_2O_6S$ requires C, 46·0; H, 3·0%); $\nu_{max.}$ (cyclohexane) 2073, 2032, 2007, 1995, and 1988 cm^{-1} (C=O); τ (100 MHz; $CDCl_3$) 8·95 (Bu^t).

5-Phenyl-4-*p*-t-butylphenyl-1,2,3-thiadiazole (2·50 g) in tetrahydrofuran (75 ml) for 24 h gave μ-[α-*phenyl*-p-*t-butyl*-(*thiophenacylidene*)]-*bis*(*tricarbonyliron*)(Fe–Fe) (9d) (1·16 g, 25%), m.p. 116—118° (from petroleum) (Found: C, 52·7; H, 3·3; S, 6·1%; *m/e* 546. $C_{24}H_{18}Fe_2O_6S$ requires C, 52·8; H, 3·3; S, 5·9%; *M*, 546); τ (100 MHz; $CDCl_3$) 8·70 (Bu^t).

4-Phenyl-5-*p*-t-butylphenyl-1,2,3-thiadiazole (1·20 g) in tetrahydrofuran (40 ml) for 24 h gave a red oil (0·270 g) which did not crystallise; the major component (>90%) was identified as μ-[α-(*t-butylphenyl*)*thiophenacylidene*]-*bis*-(*tricarbonyliron*)(Fe–Fe) (9e), *m/e* 546; τ (100 MHz; $CDCl_3$) 8·74 (Bu^t), although it could not be obtained completely free from its isomer (9d) or from 1-phenyl-2-*p*-t-butylphenylacetylene.

4,5-Diphenyl-1,2,3-selenadiazole (0·590 g), when heated under reflux for 0·5 h in dimethoxyethane (20 ml), gave μ-[α-*phenyl*(*selenophenacylidene*)]-*bis*(*tricarbonyliron*)(Fe–Fe) (10a) (0·066 g, 6%), m.p. 125° (from petroleum) (Found:

* The reported m.p. was not attained.

[26] T. Kauffmann and J. Sobel, *Chem. Ber.*, 1966, **99**, 1843; H. Wieland and H. Kloss, *Annalen*, 1929, **470**, 211.

[27] B. S. Kupin and A. A. Petrov, *J. Gen. Chem.* (*U.S.S.R.*), 1961, **31**, 2758.

C, 44·6; H, 2·0%; *m/e* 537·8339. $C_{20}H_{10}Fe_2O_6Se$ requires C, 44·7; H, 1·9%; *M*, 537·8340); $\nu_{max.}$ (cyclohexane) 2073, 2039sh, 2034, 2002sh, 1997, 1990sh, and 1984w cm^{-1} (C=O).

5-Phenyl-4-*p*-t-butylphenyl-1,2,3-selenadiazole (0·700 g) when heated under reflux for 0·5 h in dimethoxyethane (20 ml), gave μ-[α-*phenyl*-p-*t-butyl*(*selenophenacylidene*)]-*bis*-(*tricarbonyliron*)(Fe–Fe) (10b) (0·322 g, 26%), m.p. 117—119° (from petroleum) (Found: C, 48·5; H, 2·9%; *m/e* 529. $C_{24}H_{18}Fe_2O_6Se$ requires C, 48·6; H, 3·1%; *M*, 529); $\nu_{max.}$ (cyclohexane) 2067, 2032, 2028, 1998sh, 1995, and 1987w cm^{-1} (C=O); τ (100 MHz; $CDCl_3$) 8·72 (Bu^t).

4-Phenyl-5-*p*-t-butylphenyl-1,2,3-selenadiazole (0·600 g) when heated under reflux for 0·5 h in dimethoxyethane (20 ml) gave a red oil (0·340 g) which crystallised when cooled below 0°. The major component (>95%) was identified as μ-[α-p-*t-butylphenyl*(*thiophenacylidene*)]-*bis*(*tricarbonyliron*)(Fe–Fe) (10c); τ (100 MHz; $CDCl_3$) 8·76 (Bu^t); a specimen could not be obtained free from small amounts (<5%) of the isomer (10b) and of 1-phenyl-2-*p*-t-butylphenylacetylene.

Control Experiments.—Thermal stability of 5-*phenyl*-4-p-*t-butylphenyl*-1,2,3-*thiadiazole* (4d). The thiadiazole (0·5 g) was heated under reflux for 48 h in tetrahydrofuran (20 ml). Evaporation left the thiadiazole (4d). Absence of the isomeric thiadiazole (4e) in the product was shown by n.m.r. spectroscopy: τ (4d) (100 MHz; benzene) 8·89 (Bu^t) [τ (4e) 8·94]. The signals were coincident in $CDCl_3$.

Tests for equilibration of the complex (9d). (*a*) The complex (9d) (0·100 g) was heated under reflux for 48 h in tetrahydrofuran (10 ml). The solvent was evaporated off and the residue dissolved in [^{2}H]chloroform; τ (100 MHz; $CDCl_3$) 8·70 (Bu^t); there was no signal for the isomeric complex (9e) (τ 8·74).

(*b*) The complex (9d) (0·100 g) and nonacarbonyldi-iron (1·0 g) were stirred for 12 h in tetrahydrofuran (10 ml) under reflux. The mixture was evaporated, and the residue shaken with pentane (20 ml). The mixture was filtered and the filtrate evaporated to dryness. The residue was dissolved in [^{2}H]chloroform; the n.m.r. spectrum showed one sharp signal (100 MHz) at τ 8·70. Evaporation of the solution and trituration of the residue with methanol–dichloromethane gave red crystals of complex (9d), m.p. 120—122°.

Reactions of the dithiafulvene (11) *and the dithiacyclohexadiene* (12) *nonacarbonyldi-iron*. 4,5-Diphenyl-1,2,3-thiadiazole (4·0 g) in benzene (120 ml) at 80° was irradiated (Hanovia 125 W medium pressure lamp; 10 h). The mixture was filtered and the filtrate evaporated to dryness. The residue was extracted with chloroform to give a solid (3·4 g). Crystallisation from ethanol gave a mixture of tetraphenyldithiafulvene and tetraphenyl-1,4-dithiacyclohexadiene (t.l.c.) as pale yellow needles.

The mixture (0·4 g) and nonacarbonyldi-iron (1·8 g) were heated in tetrahydrofuran (20 ml) under reflux for 13 h. T.l.c. showed the formation of an iron complex which was readily distinguishable from the carbene complex (9a); the latter was shown to be absent in the product mixture.

We thank the S.R.C. for financial support, and Mr. S. A. Minns for experimental assistance.

[2/815 *Received*, 10*th April*, 1972]