Electrochemical Reactions of Fluoro-compounds. Part II.[1] The Preparation of Substituted Fluoro-aromatic Derivatives

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2,4,5,6-Tetrafluoro-1,3-phenylenediamine has been prepared by the electrochemical reduction of 1-amino-3-imino-heptafluorocyclohex-1-ene at a mercury cathode. Similarly, by reduction of other amino-imino-fluorocyclohex-1-enes and aminoheptafluorocyclohexenones, 2-trifluoromethyl-4,5,6-trifluoro-1,3-phenylenediamine, 1-amino-2,4,5,6-tetrafluorophenol, and 1-isopropylamino-2,4,5,6-tetrafluorophenol were obtained. The reduction of 1-methylamino-3-methyliminoheptafluorocyclohex-1-ene was anomalous, and gave 2,5,6-trifluoro-4*H*-*NN'*-dimethyl-1,3-phenylenediamine. 1-Amino-3-imino-pentafluorocyclopent-1-ene gave 1,3-diamino-3*H*-pentafluorocyclopent-1-ene without loss of fluorine. The polarographic reduction of the cyclohexene derivatives and some mono substituted heptafluorocyclohexa-1,3 and 1,4-dienes has also been investigated, and changes in $E_{\frac{1}{2}}$ discussed in terms of the Hammett σ_p function.

In a previous paper[1] we described the polarography and controlled-potential reduction of a number of highly fluorinated cyclohexa-1,3- and cyclohexa-1,4-dienes. From the results it was concluded that a similar electrode process occurred for both classes of diene, with controlled-potential reduction giving one product, the corresponding fluoroaromatic, in high yield, obtained by the loss of two fluoride ions from the diene by a 1,2- or 1,4-loss of F^-. We now describe the polarography and controlled-potential reduction of other substituted fluorocyclohexadienes, amino-imino-fluorocyclohexenes, amino-fluorocyclohexenones, and an amino-imino-fluorocyclopentene.

Some of the starting materials for polarography and large-scale electrochemical reduction were prepared by methods already described in the literature [compounds (I)—(VII) [2-4]] (VIII), (IX) and (XI) were prepared by treating the corresponding perfluoro-olefin with methylamine and ammonia according to the method previously used for (V).[4,5] Compound (X) was obtained by the hydrolysis of (IX) with dilute hydrochloric acid as used for the synthesis of (VI),[4] and (XII) and (XIII) were prepared by the reaction between ethoxide ion and octafluorocyclohexa-1,4- and -1,3-dienes respectively.[2] The structures of all these compounds were confirmed by chemical analysis and i.r., ^{19}F, and ^1H, n.m.r. spectroscopy. In addition, the structure of the 2-methoxy- and 2-ethoxy-dienes has been confirmed[2] by the formation of the correct Diels–Alder adduct.

The polarographic results (Tables 1 and 2) obtained

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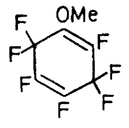
[1] Part I, A. M. Doyle, A. E. Pedler, and J. C. Tatlow, *J. Chem. Soc.* (*C*), 1968, 2740.

[2] A. Clayton, R. Stephens, submitted for publication; D. J. Dodsworth, R. Stephens, and J. C. Tatlow, unpublished work.

[3] J. Riera and R. Stephens, *Tetrahedron*, 1966, **22**, 2555.

[4] P. Robson, J. Roylance, R. Stephens, J. C. Tatlow, and R. E. Worthington, *J. Chem. Soc.*, 1964, 5748.

[5] P. A. Carter, Ph.D. Thesis, University of Birmingham, 1964.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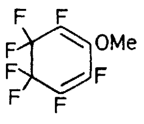
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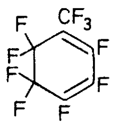
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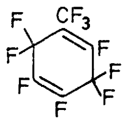
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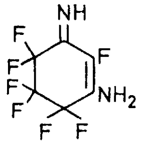
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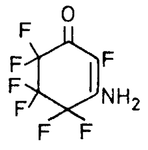
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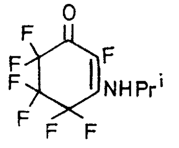
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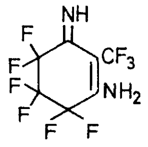
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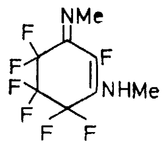
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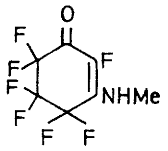
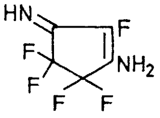

(X)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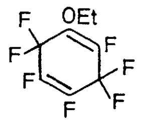
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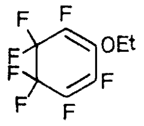

(XIII)

for the methoxy- [(I), and (II)], ethoxy- [(XII) and (XIII)] and trifluoromethyl- [(III) and (IV)] heptafluorocyclohexa-1,3- and -1,4-dienes are in accord with the results already reported for other fluorocyclohexadienes.[1]

Thus the values of $nD^{\frac{1}{2}}$ obtained using tetramethylammonium chloride as supporting electrolyte are in the range 2·7—3·0 × 10^{-3}, indicative of a 2e reduction process: this was confirmed by the preparative controlled-potential reduction of 2-ethoxyheptafluorocyclohexa-1,3-diene which gave 2,3,4,5,6-pentafluorophenetole in high yield. The values of $n\alpha$ for the 1,3-dienes and 1,4-dienes are in the range 0·61—0·67 and 0·48—0·52 respectively, in agreement with values previously reported for other fluoro-dienes. The half-wave potentials were independent of pH.

TABLE 1

		$E_{\frac{1}{2}}$ ± 0·01 V			
			M-Potassium acetate		
Compd.	Capillary	0·4M-NMe_4Cl	pH 7·5	pH 9·5	pH 11·5
(I)	b	−1·68			
(II)	b	−1·39			
(III)	b	−0·87	−1·07	−1·07	−1·08
(IV)	a	−1·14			
(V)	b	−1·24	−0·88	−1·23	−1·26
(VI)	b	−1·03	−1·07	−1·08	−1·09
(VII)	b	−1·00	−1·02	−1·04	−1·05
(VIII)	b	−1·33	−1·36	−1·42	−1·42
(IX)	b	−1·31	−0·80	−1·09	−1·12
(X)	b	−1·02	−1·07	−1·07	−1·08
(XI)	b	−1·51			
(XII)	b	−1·75			
(XIII)	a	−1·40			

All the mono-substituted fluoro-dienes we have investigated contain two non-equivalent CF_2 groups, from either of which a fluorine atom may be lost in the initial step. Substitution of a group R for fluorine on one of the double bonds of octafluorocyclohexa-1,4-diene could be expected to influence the polarographic behaviour of the two CF_2 groups differently, that attached to C-1 being affected largely by the inductive, and that at C-2 by both the inductive and resonance, properties of the group relative to fluorine.

If reduction of the CF_2 group at C-1 is potential determining then since the groups substituted for fluorine exert a smaller inductive effect, $E_{\frac{1}{2}}$ should become more negative for all the substituted polyfluoro-1,4-dienes. Table 1 shows that this is not observed. However, if reduction of the difluoromethylene group

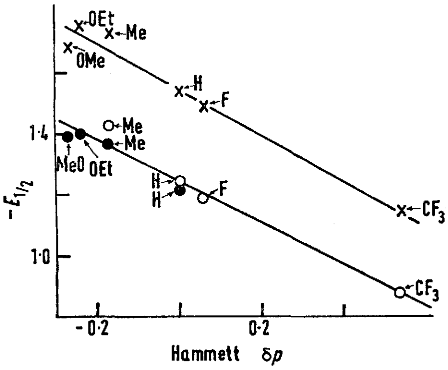
TABLE 2

	0·4M-NMe_4Cl			M-Potassium acetate					
				pH 7·5		pH 9·5		pH 11·5	
Compd.	i_d/C (μA. mM^{-1})	$nD^{\frac{1}{2}} \times 10^3$	$n\alpha$	i_d/C (μA. mM^{-1})	$nD^{\frac{1}{2}} \times 10^3$	i_d/C (μA. mM^{-1})	$nD^{\frac{1}{2}} \times 10^3$	i_d/C (μA. mM^{-1})	$nD^{\frac{1}{2}} \times 10^3$
(I)	3·9	3·0	0·48						
(II)	3·7	2·8	0·67						
(III)	3·6	2·7							
(IV)	3·8	2·7	0·52						
(V)	7·8	6·3	0·61	8·0	6·4	6·8	5·5	6·4	5·1
(VI)	6·8	5·4	0·63	7·7	6·1	7·7	6·1	7·7	6·1
(VII)	8·2	6·5	0·65	9·0	7·1	9·0	7·1	9·0	7·1
(VIII)	7·1	5·7	0·57	7·5	5·9	7·5	5·9	7·5	5·9
(IX)	7·8	6·2	0·48	9·3	6·3	6·8	5·4	6·4	5·1
(X)	6·4	5·1	0·66	8·6	6·7	8·6	6·7	8·6	6·7
(XI)	3·9	3·1	0·58						
(XII)	3·4	2·7	0·48						
(XIII)	3·8	2·7	0·61						

at C-2 is potential determining a correlation between the Hammett σ_p function and $E_{\frac{1}{2}}$ might be expected.[6a] The Figure is a plot of σ_p *vs.* $E_{\frac{1}{2}}$ [6b] for the 1,4-dienes investigated and shows a good correlation from which $\rho_\pi = 0{\cdot}77$ V, where $\Delta E_{\frac{1}{2}} = \rho_\pi \sigma_p$.

Similar correlations have been previously observed between polar inductive (σ^I) and Hammett (σ_p) formations and reactivity of unsaturated aliphatic compounds. Thus, the half-wave potentials for the reduction of substituted allyl bromides, $RCH{=}CH{-}CH_2Br$ (R = Me, H, Cl, or Br) have been correlated with σ^I values,[6a,7] although use of σ_p values gives a better correlation. In addition a good correlation has been found to exist between σ_p constants and the p*K* values of trans-3-substituted acrylic acids.[8]

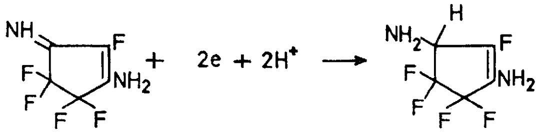
Similar arguments may be applied to the effect of substituents on the reduction of 1- and 2-substituted 1,3-dienes. The CF_2 group attached at C-1 in 1-substituted and at C-4 in 2-substituted polyfluoro-1,3-dienes is affected by the relative inductive properties of the substituent. The CF_2 group at C-4 in 1-substituted and at C-1 in 2-substituted polyfluoro-1,3-dienes is situated such that combined inductive and resonance effects can operate. A plot of $E_{\frac{1}{2}}$ *vs.* σ_p is shown in the Figure for the substituted 1,3-dienes, for which a good correlation is observed, giving $\rho_\pi = 0{\cdot}69$ V.



Plot of Hammett σ_p function *vs.* $E_{\frac{1}{2}}$ for series of polyfluorodienes: ×, 1-substituted polyfluoro-1,4-dienes, ○, 1-substituted polyfluoro-1,3-dienes, ●, 2-substituted polyfluoro-1,3-dienes. Hammett σ_p data from ref. 12

The common correlation curve for the 1- and 2-substituted 1,3-dienes is not altogether surprising even though the most easily reducible CF_2 groups are *para* and *ortho* respectively to the substituent, since it is commonly accepted that the Hammett σ_p and σ_o constants (excluding steric effects) are similar in value. The greater ease of reduction of the polyfluoro-1,3-dienes ($E_{\frac{1}{2}} \sim 0{\cdot}3$ less negative than the corresponding 1,4-diene) may then be ascribed to the inductive effect of vicinal CF_2 group in the 1,3-dienes.

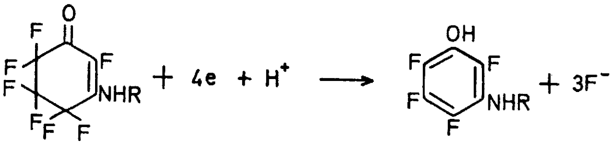
The polarographic behaviour and results of the preparative-scale controlled-potential reduction of the cyclopentene derivative (XI), the amino-cyclohexenones (VI), (VII) and (X), and the amino-imino-cyclohexenes (V), (VIII), and (IX) are complex. The value of $nD^{\frac{1}{2}}$ in tetramethyl ammonium chloride solution of 1-amino-3-imino-pentafluorocyclopent-1-ene is $3{\cdot}1 \times 10^{-3}$ ($n\alpha = 0{\cdot}58$), indicative of a 2e reduction. This was confirmed by controlled-potential reduction at $-1{\cdot}75$ V, which formed 1,3-diamino-3*H*-pentafluorocyclopent-1-ene, according to equation (1):



(1)

The diamino-compound was identified by elemental analysis and i.r., u.v., and mass spectrometry. The ^1H and ^{19}F n.m.r. were consistent with the proposed structure.

Polarography of the aminocyclohexenones (VI), (VII), and (X) in tetramethylammonium chloride solution gave values of $nD^{\frac{1}{2}}$ in the range $5{\cdot}1$—$6{\cdot}5 \times 10^{-3}$ indicative of a 4e reduction. The order of the $E_{\frac{1}{2}}$ values was that given by the relative electron-denoting properties of the *N*-substituted alkyl group (H < Me < Pr^i), the isopropyl derivative being the most readily reduced. The values of $E_{\frac{1}{2}}$ measured in potassium acetate solution pH 7·5, 9·5, and 11·5 varied little although tending to become more negative with increasing pH. Controlled-potential reduction of compounds (VI) and (VII) gave rise to the corresponding aminophenols according to the overall equation (2). Thus, 3-aminoheptafluorocyclohex-2-enone (VI) gave, by a four-electron reduction, as indicated polarographically, 3-amino-2,4,5,6-tetrafluorophenol, in high yield. Elemental analysis confirmed the empirical formula, and the structure was determined by ^1H and ^{19}F n.m.r. spectroscopy. The dissociation constant of the phenol was found to be $0{\cdot}72 \times 10^{-7}$ by potentiometric titration. Likewise, reduction of 3-isopropylaminoheptafluorocyclohex-2-enone (VII) gave 3-isopropylamino-2,4,5,6-tetrafluorophenol, the structure being confirmed by elemental analysis and ^1H and ^{19}F n.m.r. spectroscopy. The dissociation constant of this phenol was found to be $0{\cdot}27 \times 10^{-7}$.



(2)

The polarographic behaviour and controlled-potential reduction of 2-chlorocyclohexanone[9] and other 2-halogenocyclohexanones[10] has been studied previously.

[6a] P. Zuman, 'Substituent Effects in Organic Polarography,' Plenum Press, New York, 1967.

[6b] G. B. Barlin and D. D. Perrin, *Quart. Rev.*, 1966, **120**, 75.

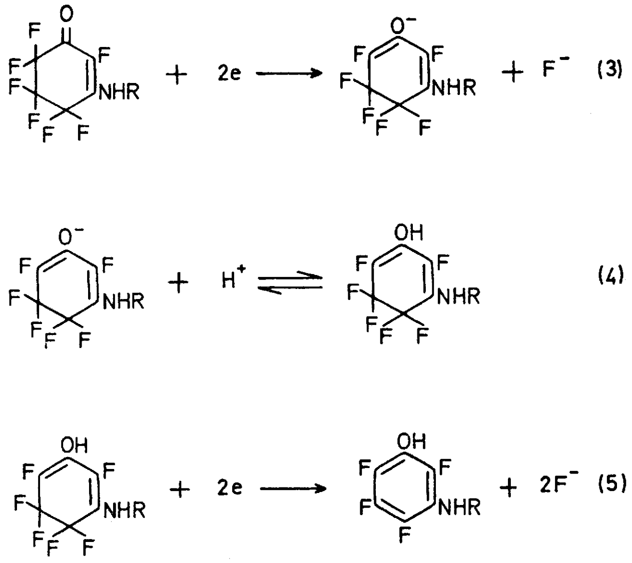
[7] M. Kleine-Peter, *Compt. rend.*, 1955, **240**, 517.

[8] M. Charton and H. Meislich, *J. Amer. Chem. Soc.*, 1958, **80**, 5940.

[9] P. J. Elving and R. E. Van Atta, *J. Electrochem. Soc.*, 1956, **103**, 676.

[10] A. M. Wilson and N. L. Allinger, *J. Amer. Chem. Soc.*, 1961, **83**, 1999.

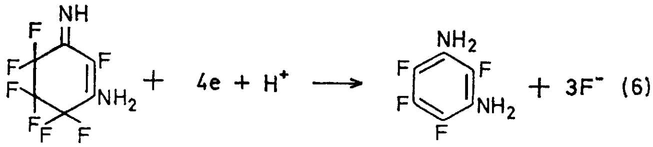
The results indicated a 2e-reduction of the chloro-compound to cyclohexanone, the reaction proceeding *via* the synchronous addition of 2 electrons and loss of Cl^- as the potential-determining step, followed by reaction of the carbanion with a hydrogen ion to form cyclohexanone. To account for our results we propose the mechanism shown in the Scheme where reaction (3) or reactions (3) and (4) in combination are potential determining. The reduction of the conjugated diene formed in reaction (4) is analogous to the reduction of the other conjugated dienes we have investigated.[1] The magnitude of the changes in $E_{\frac{1}{2}}$ with structure and pH suggests that the protonated form of the amino-cyclohexenones only participates to a small extent in the reduction process.



R = H,Me, or Pr^i

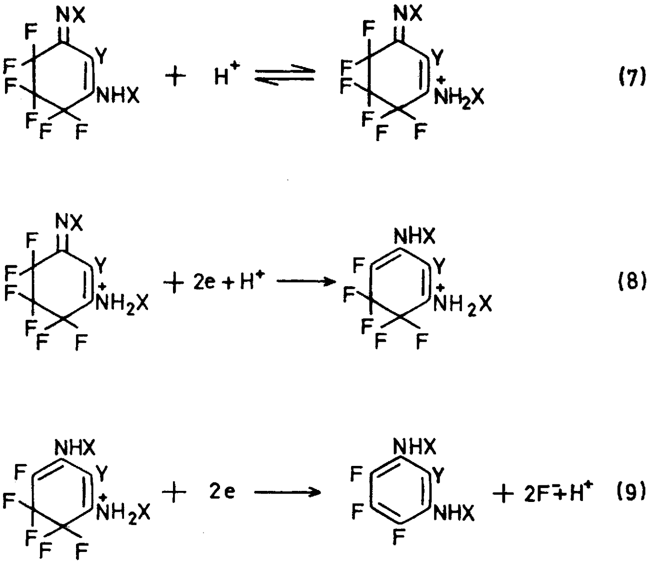
The electrochemical behaviour of the amino-imino-cyclohex-1-ene derivatives (V), (VIII), and (IX) is comparable with that of the amino-fluorocyclohexenones. Thus the values of $nD^{\frac{1}{2}}$ are in the range 5·7—6·3 × 10^{-3}, consistent with a 4e reduction, with $n\alpha$ = 0·48—0·61. The half-wave potential of 1-amino-3-imino-2-trifluoromethylhexafluorocyclohex-1-ene (VIII) is unexpectedly more negative than that of 1-amino-3-iminoheptafluorocyclohex-1-ene (V) and *NN'*-dimethylation of compound (V) results in $E_{\frac{1}{2}}$ becoming more positive. However, the half-wave potentials of compounds (V), (VIII), and (IX) are markedly pH dependent, the effect being greatest for compounds (V) and (IX). The shape of the wave front is also dependent on the pH of the electrolyte solution.

Controlled-potential reduction of 1-amino-3-imino-heptafluorocyclohex-1-ene (V) gave rise to 2,4,5,6-tetra-fluoro-1,3-phenylenediamine as the sole product in good yield. The total number of coulombs passed corresponded to approximately 90% of a four electron/mole reduction according to equation (6). Similarly, reduction of 1-amino-2-trifluoromethyl-3-iminohexafluorocyclohex-1-ene (VIII) gave, after passing 87% of the theoretical current required, 2-trifluoromethyl-4,5,6-trifluoro-1,3-phenylenediamine. Elemental analysis confirmed the molecular formula, with the ^1H and ^{19}F n.m.r. spectra in agreement with the assigned structure.



The controlled-potential reduction of 1-methyl-amino-3-methyliminoheptafluorocyclohex-1-ene (IX) was anomalous. Although $nD^{\frac{1}{2}} = 6{\cdot}2 \times 10^{-3}$, indicating a 4 electron reduction, electrolysis of a solution of the cyclohexene required more than the theoretical number of coulombs for a four-electron reaction. The product of the controlled-potential reduction was identified by chemical analysis, mass spectrometry, and ^1H and ^{19}F n.m.r. spectroscopy as 2,5,6-trifluoro-4*H*-*NN'*-di-methyl-1,3-phenylenediamine, corresponding to a 6-electron/mole reaction.

The mechanism that we propose for the reduction of compounds (V), (VIII), and (IX) is similar to that suggested for the reduction of the aminocyclohexenones:



X = H or Me, Y = F
X = H, Y = CF_3

Although the actual ionization state of the electro-active species is unknown, from the form of the $E_{\frac{1}{2}}$ = *f*(pH) relationship it is likely that the reduction of a protonated form of the substrate is involved. However, the change in the shape of the polarographic wave front with pH suggests that the neutral species may also be involved.

EXPERIMENTAL

N.m.r. spectra were recorded on samples dissolved in [$^2H_6$]acetone unless otherwise stated. All data are quoted on the δ scale with high-field (low frequency) shifts negative, the reference standards being (δ = 0·0) Me_4Si and CCl_3F for ^1H and ^{19}F spectra respectively. The n.m.r. spectra for compounds (VIII) to (XIX) are given in Table 3, and are consistent with the proposed structures.

Known starting materials for reduction and polarographic studies were prepared by published methods. These compounds were 1-methoxyheptafluorocyclohexa-1,4-diene (I),[2] 2-methoxyheptafluorocyclohexa-1,3-diene (II),[2] 1-trifluoromethylheptafluorocyclohexa-1,3- (III)-[3] and -1,4-dienes (IV),[3] 1-amino-3-iminoheptafluorocyclohex-1-ene (V),[4] 3-aminoheptafluorocyclohex-2-enone (VI),[4] and 3-isopropylaminoheptafluorocyclohex-2-enone (VII).[4] The preparation of new compounds is described below.

Table 3

Compound	^{19}F n.m.r. spectra: Chemical shifts (−δ)	Intensity ratios	^1H n.m.r. spectra: Chemical shifts (δ)	Intensity ratios
(VIII)	56·9 (singlet), 117·3, 122·4, 136·8 (quintet)	3 : 2 : 2 : 2	7·40, 10·70	2 : 1
(IX)	116 (v. broad peak), 134·3 (quintet), 154·0 (singlet)	4 : 2 : 1	3·35 (doublet), 6·1 (v. broad signal)	6 : 1
(X)	114·3, 123·4, 133·3, 165·1	2 : 2 : 2 : 1	3·35 (doublet), 7·95 (singlet)	3 : 1
(XI)	119·97, 159·57	4 : 1	7·62	
(XII in CCl_4)	110·1, 157·1, 158·9, 163·3	4 : 1 : 1 : 1	1·42, 4·4 (quartet of doublets)	3 : 2
(XIII in CCl_4)	122·3, 124·4, 147·0 (triplet), 166·0, 168·5	2 : 2 : 1 : 1 : 1	1·38 (triplet), 4·31	3 : 2
(XIV)	160·9, 168·9, 169·8, 174·6	1 : 1 : 1 : 1	4·62, 8·4	2 : 1
(XV)	156·8, 165·6, 168·5, 171·6	1 : 1 : 1 : 1	1·2, 3·76, 8·9	6 : 2 : 1
(XVI)	55·1 (singlet), 158·0 (triplet), 172·5 (doublet)	3 : 1 : 2	4·9	
(XVII)	140 (quintet), 158 (broad singlet), 167·0 (doublet)	1 : 1 : 1	2·7, 2·9, 3·5, 5·7 (doublet of triplets)	3 : 3 : 2 : 1
(XVIII)	A series of AB signals from 104—130 (due to $-CF_2-$ groups), intensity ratio 4, and from 147—150, intensity ratio 1		4·4 (No signals characteristic of $-CHF-$ observed)	
(XIX in CCl_4)	Two sets of signals in the intensity ratio 2 : 3 at 157·9 and 165·2. The spectrum was not typical of pentafluoroaromatics (A_2B_2M), but as in pentafluoroanisole there was near coincidence of the 4-F with the 3-F and 5-F signals		4·25 (quartet), 1·43 (triplet)	3 : 2

1-*Amino*-3-*imino*-2-*trifluoromethylhexafluorocyclohex*-1-*ene* (VIII).—(After P. A. Carter, C. R. Patrick, and J. C. Tatlow, unpublished work.[5]) Ammonia was passed into an ice-cold solution of dodecafluoromethylcyclohex-1-ene (5 g.) in ether (80 ml.) for 6 hr. Water (100 ml.) was then added, and the water layer was separated, and extracted with ether (3 × 30 ml.). The ethereal extract and the original ether layer were combined, dried ($MgSO_4$), filtered, and evaporated to give a pale yellow crystalline solid which was recrystallized from carbon tetrachloride to give 1-*amino*-3-*imino*-2-*trifluoromethylhexafluorocyclohex*-1-*ene*, (2·9 g), m.p. 101—102° (Found: C, 29·6; H, 1·1; N, 9·6. $C_7H_3F_9N_2$ requires C, 29·3; H, 1·0; N, 9·7%); $\nu_{max.}$ 3450 and 3270 cm^{-1} (N–H stretch) and 1665 cm^{-1} (C=C stretch); $\lambda_{max.}$ (EtOH) 2750 Å (ε 0·55 × 10^4) (–C=C–C=N–).

The structure assigned to the compound was further confirmed by oxidation with potassium permanganate to give hexafluoroglutaric acid, showing that the compound contained the $[CF_2]_3$ grouping.

1-*Methylamino*-3-*methyliminoheptafluorocyclohex*-1-*ene* (IX).—Decafluorocyclohexene (42·0 g.) was added slowly to aqueous methylamine (30%, 50 ml.) at 0° and the mixture was stirred for 30 min. The product was extracted with ether (3 × 100 ml), and the ethereal extract was washed with water, dried ($MgSO_4$), filtered, and evaporated. The product (31·6 g.) was recrystallized from aqueous ethanol to yield 1-*methylamino*-3-*methylimino*-*heptafluorocyclohex*-1-*ene* (26·5 g.), m.p. 83° ($C_8H_7F_7N_2$ requires C, 36·4; H, 2·7. Found: C, 36·4; H, 2·7%); $\lambda_{max.}$ = 3070 Å (ε 2·23 × 10^4).

3-*Methylaminoheptafluorocyclohex*-2-*enone* (X).—1-Methylamino-3-methyliminoheptafluorocyclohex-1-ene (10·5 g.) was shaken with aqueous hydrochloric acid (2N; 350 ml.) until complete dissolution occurred. The solution was set aside at room temperature for 48 hr. after which time the precipitate (8·6 g) was separated. Recrystallization of the precipitate from aqueous ethanol gave 3-*methylaminoheptafluorocyclohex*-2-*enone* (7·7 g.), m.p. 121° (Found: C, 33·3; H, 1·6; N, 5·9. $C_7H_4F_7NO$ requires C, 33·5; H, 1·6; N, 5·6%); $\lambda_{max.}$ (EtOH) 3130 Å (ε 2·73 × 10^4); $\nu_{max.}$ 1600 cm^{-1} (C=O).

1-*Amino*-3-*iminopentafluorocyclopent*-1-*ene* (XI).—A slow stream of gaseous ammonia was bubbled through octafluorocyclopentene (9·4 g.) in ether (100 ml.) for 2 hr. Water (100 ml.) was added and the ether layer was separated. The aqueous layer was extracted with ether, and the ethereal extracts were combined with the separated ether layer. The dried ($MgSO_4$) ethereal solution was evaporated and the residue (7·35 g.) was recrystallized from carbon tetrachloride–benzene to give 1-*amino*-3-*iminopentafluorocyclopent*-1-*ene*, (5·88 g.), m.p. 116° (Found: C, 32·1; H, 1·6; N, 15·1. $C_5H_3F_5N_2$ requires C, 32·3; H, 1·6; N, 15·1%.

1-*Ethoxyheptafluorocyclohexa*-1,4-*diene* (XII).—To octafluorocyclohexa-1,4-diene (23·71 g.) and potassium hydroxide (5·93 g.) was added slowly dry ethanol (5·39 g.), with stirring and cooling. The reaction mixture was stirred at room temperature for 1 hr. after which time the fluorocarbon layer was separated, washed (H_2O), and dried ($MgSO_4$). The product (24·73 g.) was separated by preparative scale g.l.c. [dinonyl phthalate–Celite (1 : 2) at 80°] to give (i) a mixture (3·1 g.) which was not further investigated and (ii) 1-*ethoxyheptafluorocyclohexa*-1,4-*diene* (16·0 g.) (Found: C, 38·9; H, 2·0; F, 52·6%; $C_8H_5F_7O$ requires C, 38·4; H, 2·0; F, 53·2%).

The mass spectrum had a top mass peak of 250 and a fragmentation pattern consistent with the proposed structure; $\lambda_{max.}$ (EtOH) 2290 Å (ε 1·6 × 10^3) consistent with an ethoxy-group attached to a double bond, and a 1,4-diene.

2-*Ethoxyheptafluorocyclohexa*-1,3-*diene* (XIII).—Dry ethanol (5·30 g.) was added slowly, with stirring and cooling to octafluorocyclohexa-1,3-diene (23·27 g.) and potassium hydroxide (5·93 g.). At the end of the addition the mixture was stirred for 1 hr. at room temperature, after which time the fluorocarbon layer was separated, washed (H_2O) and dried ($MgSO_4$). The product (24·54 g.) was separated by preparative scale g.l.c. into (i) starting material (0·61 g.), (ii) a mixture (1·80 g.) and (iii) 2-*ethoxyheptafluorocyclohexa*-1,3-*diene* (16·43 g.) (Found: C, 38·7; H, 1·7; F, 53·0. $C_8H_5F_7O$ requires C, 38·4; H, 2·0; F, 53·2%).

The mass spectrum gave a top mass peak of 250 and a cracking pattern consistent with the proposed structure; $\lambda_{max.}$ (EtOH) 2720 Å (ε 3·2 × 10³) indicating that the compound was conjugated.

Controlled-potential Reductions.—The apparatus and technique for controlled-potential reductions was similar to that previously used.[1] Reductions were performed with a mercury cathode, the electrolyte being a mixture of ethanol (900 ml.), water (600 ml.), and AnalaR potassium acetate (400 g./l.) the pH of which was adjusted to a suitable value with glacial acetic acid. After reduction at a fixed cathode potential (measured against a saturated calomel electrode), the catholyte was evaporated under reduced pressure to remove ethanol and extracted with ether (7 × 150 ml.). The ethereal extract was washed with dilute aqueous sodium hydrogen carbonate (2 × 100 ml.) and water (100 ml.) and then dried ($MgSO_4$) and evaporated. The residue was purified by g.l.c. separation, sublimation, and recrystallization or distillation as appropriate. Details of the controlled-potential reductions are given in Table 4.

TABLE 4

Compound	Wt. reduced (g.)	pH	No. of electrons	Coulombic yield (%)	Cathode potential (v)	Crude product (g.)	Pure product (g.)	Purification method	Products
(V)	7·53	9·8	4	87	−1·50	3·89	2·67	[a] H_2O	2,4,5,6-Tetrafluoro-1,3-phenylenediamine
(VI)	6·00	7·8	4	90	−1·40	1·94	1·24	[a] CCl_4	1-Amino-2,4,5,6-tetrafluorophenol
(VII)	6·88	7·8	4	98	−1·40	2·47	1·53	[a] H_2O	1-Isopropylamino-2,4,5,6-tetrafluorophenol
(VIII)	6·88	8·5	4	87	−1·50	3·30	2·02	*b*	4,5,6-Trifluoro-2-trifluoromethyl-1,3-phenylenediamine
(IX)	5·73	7·5	6	78	−1·20	2·16	1·78	[a] H_2O–EtOH	2,5,6-Trifluoro-4*H*-*NN'*-dimethyl-1,3-phenylenediamine
(XI)	6·11	9·5	2	98	−1·75	1·56	1·28	[a] CCl_4	1,3-Diamino-3*H*-pentafluorocyclopent-1-ene
(XIII)	7·50	9·0	2	90	−1·65	4·10	3·14	*c*	2,3,4,5,6-Pentafluorophenetole + 0·14 g. (XIII)

[a] Sublimation followed by recrystallization under N_2 from the stated solvent. [b] Distillation under reduced pressure. [c] G.l.c. separation.

Reduction of 1-*Amino*-3-*iminoheptafluorocyclohex*-1-*ene* (V).—The title compound was reduced to give 2,4,5,6-tetrafluoro-1,3-phenylenediamine, m.p. 127—128°, identified by a comparison of its i.r., ^{19}F and, ^1H n.m.r. spectra with those of an authentic sample.[11]

Reduction of 3-*Aminoheptafluorocyclohex*-2-*enone* (VI).—The ketone was reduced to give 1-*amino*-2,4,5,6-*tetrafluorophenol* (XIV); m.p. 95° (Found: C, 40·0; H, 1·7; N, 7·6; F, 41·5. $C_6H_3F_4NO$ requires C, 39·8; H, 1·7; N, 7·7; F, 42·0%). A solution of the phenol (0·0254 g.) in aqueous ethanol (20 ml., 50%) was potentiometrically titrated against 1·03 × 10⁻² N-aqueous sodium hydroxide to give an equivalent weight of 184 ($C_6H_3F_4NO$ requires 181). From the pH at half neutralization the dissociation constant was calculated to be 0·72 × 10⁻⁷.

Reduction of 3-*Isopropylaminoheptafluorocyclohex*-2-*enone* (VII).—The named compound was reduced to yield 1-*isopropylamino*-2,4,5,6-*tetrafluorophenol* (XV), m.p. 112—113° (Found: C, 48·8; H, 4·4; N, 5·9; F, 33·6. $C_9H_9F_4NO$ requires C, 48·4; H, 4·0; N, 6·3; F, 34·1%. A solution of the phenol (0·030 g.) in aqueous ethanol (20 ml., 50%) was potentiometrically titrated against 0·826 × 10⁻² N-sodium hydroxide solution to give an equivalent weight of 233 ($C_9H_9F_4NO$ requires 223). From the pH at half neutralization the dissociation constant was found to be 0·28 × 10⁻⁷.

Reduction of 1-*Amino*-3-*imino*-2-*trifluoromethylhexafluorocyclohex*-1-*ene* (VIII).—The title compound was reduced to yield 4,5,6-*trifluoro*-2-*trifluoromethyl*-1,3-*phenylenediamine* (XVI), m.p. 36—37°. The compound was extremely unstable, and oxidized rapidly in dry air (Found: C, 35·9; H, 1·9; F, 50·2. $C_7H_4F_6N_2$ requires C, 36·5; H, 1·7; F, 49·6%). The mass spectrum showed a top mass peak of 230 and a cracking pattern consistent with the proposed structure.

Reduction of 1-*Methylamino*-3-*methyliminoheptafluorocyclohex*-1-*ene* (IX).—The title compound was reduced to give 2,5,6-*trifluoro*-4H-NN'-*dimethyl*-1,3-*phenylenediamine* (XVII), m.p. 90—92° (Found: C, 50·5; H, 4·7; N, 14·5. $C_8H_9F_3N_2$ requires: C, 50·5; H, 4·7; N, 14·7%). The mass spectrum showed a top mass peak of 190 and a cracking pattern consistent with the proposed structure.

Reduction of 1-*Amino*-3-*iminopentafluorocyclopent*-1-*ene* (XI).—The compound was reduced to yield 1,3-*diamino*-3H-*pentafluorocyclopent*-1-*ene* (XVIII), m.p. 70—72° (Found: C, 32·2; H, 3·0; N, 14·8. $C_5H_5F_5N_2$ requires C, 31·9; H, 2·7; N, 14·9%). Mass spectrometry gave a top mass peak of 188, with a cracking pattern consistent with the proposed structure; $\nu_{max.}$ 1735s cm⁻¹ ($C{=}C{<}F$).

Reduction of 2-*Ethoxyheptafluorocyclohexa*-1,3-*diene* (XIII).—The compound was reduced to give (i) 2-ethoxyheptafluorocyclohexa-1,3-diene (0·14 g.) and (ii) 2,3,4,5,6-pentafluorophenetole (XIX) (3·14 g.) (Found: C, 45·5; H, 2·6; F, 45·0. $C_8H_5F_5O$ requires C, 45·3; H, 2·4; F, 44·8%). The mass spectrum indicated a molecular weight of 212 and gave a cracking pattern consistent with the proposed structure. The i.r. spectrum was identical with that of the product, b.p. 152—153°, obtained by heating hexafluorobenzene under reflux with sodium ethoxide in ethanol.

Polarography.—Polarographic measurements were made

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[11] W. L. Reilly and H. C. Brown, *J. Amer. Chem. Soc.*, 1956, **78**, 6032.

automatically using a Polariter PO4 polarograph: half-wave potentials and diffusion currents were measured at room temperature against a saturated calomel electrode at depolarizer concentrations of up to 3·0 mM in two electrolyte systems. These were 0·4 m tetramethyl ammonium chloride (B.D.H. polarographic grade) in ethanol–water (3 : 2, pH 7) and M-potassium acetate (AnalaR grade) in the same solvent. In the latter electrolyte half-wave potentials were measured at pH 7·5, 9·5, and 11·5 (adjusted with acetic acid), pH values not corrected for the nonaqueous solution error. Table 1 gives values of the half-wave potentials at 1 mM concentration of depolarizer and Table 2 values of i_d/C, $nD^{\frac{1}{2}}$, and $n\alpha$ (the symbols having their usual significance). Values of $nD^{\frac{1}{2}}$ were obtained from the Ilkovic equation and $n\alpha$ from the slope of the log $[i/(i_d - i)]$ *vs.* voltage curves. Capillaries a and b had $m^{\frac{2}{3}}\tau^{\frac{1}{6}} = 2{\cdot}28$ and 2·08 $\text{mg}^{\frac{2}{3}}.\ \text{sec.}^{-\frac{1}{2}}$, with $m = 2{\cdot}32$ and 2·23 mg. sec.^{-1} and $\tau = 4{\cdot}76$ and 3·26 sec. respectively. All polarograms were done in the presence of 0·01% gelatine.

The polarograms of 1 methoxy- (I), and 1-ethoxyheptafluorocyclohexa-1,4-diene (XII), 2-methoxy- (II), and 2-ethoxyheptafluorocyclohexa-1,3-diene (XIII), and 1-trifluoromethyl-heptafluorocyclohexa-1,4-diene (IV) gave simple two-electron waves in tetramethylammonium chloride solution. In the same solution 1-trifluoromethylheptafluorocyclohexa-1,3-diene (III) gave a wave showing a tendency for the formation of a maximum and a point of inflexion indicative of two one-electron waves of similar $E_{\frac{1}{2}}$; no separation of the waves was possible. With potassium acetate solution all the dienes gave a normal two electron wave with $E_{\frac{1}{2}}$ independent of pH.

Compounds (V)—(XI) gave well defined waves in 0·4M-tetramethylammonium chloride solution. The ketones [(VI), (VII), and (X)] also gave good waves in potassium acetate solution, $E_{\frac{1}{2}}$ showing a small shift to more positive potentials at lower pH, with a slight maximum at concentrations of depolarizer above 1 mM. The amino-imino-compounds [(V) and (VIII)] in potassium acetate solution gave a single well defined wave at pH 9·5 and 11·5, although at pH 7·5 the waves were shallow and drawn out. Compound (IX) gave a sharp wave at pH 7·5, with a shallow wave at pH 9·5 and 11·5. The $E_{\frac{1}{2}}$ values of compounds (V), (VII), and (IX) all showed a pronounced shift to more positive potentials at lower pH.

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