TABLE I

	K₄Fe(CN)₆		K₃Fe(CN)₆			Temperature dependence
Position	Width[a]	Position	Width[a]	Chemical shift	K₃Fe(CN)₆ (10–80°)	
-0.7 ± 0.3^{b}	3.0 ± 0.2	-11.6 ± 0.2^{b}	2.5 ± 0.2	10.9 ± 0.2	$+3.3 \times 10^{3}$ gauss deg.	
$+0.9 \pm 0.5^{c}$	....	$+50 \pm 0.50^{c}$	....	49.2 ± 0.4	-13.7×10^{3} gauss deg.	

[a] Extrapolated to zero concentration. [b] Relative to N^{14} in pure CH_3CN; 32°. [c] Relative to C^{13} in pure C_6H_6; 32°.

is known,[1] while the ferrocyanide is diamagnetic. The measurements of the chemical shifts might lead to evaluation of the spin density distribution in the paramagnetic ion and from the line widths the mechanism and kinetics of the electron exchange between the para- and diamagnetic species can be determined. The position and width of N^{14} resonance in solutions of $K_3Fe(CN)_6$ were previously measured by Shulman[2] and his results are in fair agreement with ours. Shulman attributes the paramagnetic shift to anisotropic hyperfine interaction.

The N^{14} and C^{13} line positions and widths of approximately 0.5 M aqueous solutions of the pure compounds are given in Table I. Results are expressed in gauss, and measured in a magnetic field (H_0) of about 14 kgauss. A bulk susceptibility correction was not applied since calculation shows it to be rather small (less than the line width). Shifts to a higher magnetic field are indicated as positive. The position of the N^{14} and C^{13} resonances in the paramagnetic species is a linear function of the reciprocal of the absolute temperature and the slope is given in the last column of Table I.

The results in Table I indicate: (1) The line width of N^{14} in $K_3Fe(CN)_6$ is smaller than in $K_4Fe(CN)_6$, which means that it is completely determined by quadrupolar relaxation, since, otherwise, one would expect additional broadening due to the unpaired electron in $K_3Fe(CN)_6$. The electrical field gradient at the N nucleus seems to be larger in $K_4Fe(CN)_6$, which might be attributed either to its stronger complexation with counter-ions,[3] which affects the symmetry of the ion, or to the higher total charge of the anion. (2) Relative to line positions in the diamagnetic species, N^{14} resonance in $K_3Fe(CN)_6$ is shifted to lower field while the C^{13} resonance is shifted, considerably more, to higher field. Calculation of the hyperfine coupling constants A_i from the contact shifts[4] gives $A_{N^{14}} = 0.78$ gauss and $A_{C^{13}} = -11.8$ gauss (taking $g = 2$ and $S = ^1/_2$). Assuming equal signs and similar magnitudes of the Q-values in the expression $A_i = Q\rho_i$, we deduct that the spin density of the C^{13} would be approximately 15 times higher than on the N^{14} with opposite signs. The linear dependence of C^{13} and N^{14} resonances on the reciprocal absolute temperature shows that the shift is mainly due to the unpaired electron (paramagnetic shift).

In aqueous solutions of mixtures of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$, one N^{14} resonance is observed; hence, the electron exchange rate is fast compared to the reciprocal of the chemical shift. The line width is dependent on the concentration of the ferri- and ferrocyanide. At constant total concentration maximum width is obtained in approximately 1:1 mixtures. The position of the common line is a linear function of the mole fraction of the ferri- and ferro- in the mixture. The rate of electron exchange was evaluated from the measured line width using the fast exchange approximation for an unequal doublet with different "natural" T_2 values.[5] Assuming the reaction to be described by:

rate $= k[Fe(CN)_6^{-4}][Fe(CN)_6^{-3}]$, the value of k was found to be $(6.0 \pm 0.7) \times 10^4$ sec.$^{-1}$ M^{-1} at 32°. The range of ferri- and ferrocyanide concentrations used was 0.3–0.6 M; the error given is the standard deviation from 14 measurements. No analogous measurements with C^{13} line width were obtained because of the low S/N ratio. The rate constant obtained is in fair agreement with that obtained by Wahl and co-workers,[3,6] who studied the electron exchange by isotope labeling techniques. The advantage of n.m.r. in this study is obvious, in view of the elimination of the uncertainty in the "zero-time exchange" occurring with the isotope labeling technique,[6] while the disadvantage lies in the high concentrations that must be used. The catalytic effects of various alkali positive ions on the exchange and the temperature dependence of the reaction are presently under study.

Measurements were performed on a Varian DP60 spectrometer equipped with a V4311 4.3-Mc. fixed frequency unit for N^{14} measurements and a V4210A variable frequency unit operating at 15.0 Mc. for C^{13} measurements. Samples were contained in 15-mm. o.d. tubes. In temperature dependence studies 8 mm. o.d. tubes were used in a specially constructed dewar insert. For some C^{13} measurements $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ were prepared from C^{13}-enriched[7] KCN by a procedure similar to that given by Thompson.[8]

(6) A. C. Wahl, Z. Elektrochem., 64, 90 (1960).

(7) The authors wish to thank Professor G. Stein of the Hebrew University; Jerusalem, for kindly providing KCN enriched to 15 atom % C^{13}.

(8) R. C. Thompson, J. Am. Chem. Soc., 70, 1045 (1948).

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Long-Range Spin–Spin Coupling of Protons in Isomeric 6,7-Dichloroestrone Methyl Ethers

Sir:

Spin–spin coupling of protons, attached to carbon atoms two or more bonds apart, has been observed in a number of systems containing unsaturation.[1] The success of theoretical treatments of such unsaturated systems[2] is evident from the verification of some of their predictions by experiments.[1] The theory of spin–spin splitting does not provide a reliable basis for the prediction of long-range spin–spin coupling in saturated systems.[3]

We have observed a strong spin–spin coupling between protons attached to carbon atoms two σ-bonds

(1) For leading references, see (a) E. I. Snyder and J. D. Roberts, J. Am. Chem. Soc., 84, 1582 (1962); (b) D. J. Collins, J. J. Hobbs, and S. Sternhell, Tetrahedron Letters, 197 (1963); (c) T. A. Wittstruck, S. K. Malhotra, and H. J. Ringold, J. Am. Chem. Soc., 85, 1699 (1963); (d) J. R. Holmes and D. Kivelson, ibid., 83, 2959 (1961); (e) J. A. Elvidge and R. G. Foster, J. Chem. Soc., 590 (1963); (f) E. W. Garbisch in Abstracts of Papers presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, p. 36Q; ref. 7f and earlier references cited therein.

(2) (a) M. Karplus, J. Chem. Phys., 33, 1842 (1960); (b) R. A. Hoffman, Mol. Phys., 1, 326 (1958), and subsequent papers, see ref. 1a; (c) M. Barfield and D. M. Grant, J. Am. Chem. Soc., 85, 1899 (1963).

(3) (a) See ref. 1a, footnote 6; (b) D. R. Davies and J. D. Roberts, J. Am. Chem. Soc., 84, 2252 (1962); (c) F. A. L. Anet, ibid., 84, 747 (1962); (d) K. B. Wiberg, B. R. Lowry, and B. G. Nist, ibid., 84, 1594 (1962); (e) J. Meinwald and Y. C. Meinwald, ibid., 85, 2514 (1963), and earlier references cited therein; (f) J. I. Musher and E. J. Corey, Tetrahedron, 18, 791 (1962), have developed the theory of "virtual" long range spin–spin coupling, which does not apply to the findings reported by us, see footnote 9.

(1) F. W. Gray and W. M. Birse, J. Chem. Soc., 105, 2707 (1914).

(2) R. G. Shulman, J. Chem. Phys., 29, 945 (1958).

(3) N. Sutin, Ann. Rev. Nucl. Sci., 12, 299 (1962).

(4) D. R. Eaton, A. D. Josey, W. D. Phillips and R. E. Benson, Discussions Faraday Soc., 34, 77 (1962).

(5) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., 1959, Chapter 10.

TABLE I

N.M.R. SPECTRA OF 4-H, 6-H, 7-H, AND 8-H OF Ia AND Ib

		τ		$|J_{HH}|$ (c.p.s.)
Ia	6β-H	4.46^a	$J_{6\beta, 7\beta}$	4.0^a
	7β-H	5.43^a	$J_{6\beta, 8\beta}$	1.8^b
	4-H	$2.82;^a$ 2.9^b	$J_{6\beta, 4}$	$\leqslant 0.6^c$
			$J_{7\beta, 8\beta}$	$\leqslant 1^d$
Ib	6α-H	4.72^a	$J_{6\alpha, 7\beta}$	2.2^a
	7β-H	5.44^a	$J_{6\alpha, 4}$	$\leqslant 0.5^e$
	4-H	$3.14;^a$ 3.2^f	$J_{7\beta, 8\beta}$	$\approx 1^g$

^{a} Measured at 60 Mc./sec. ^{b} Determined by spin decoupling (at 100 Mc./sec.) of 4-H from 6-H, curve B, Fig. 1. ^{c} Estimated from pattern width (at 60 Mc./sec.) of 6-H and values of $J_{6\beta,7\beta}$ and $J_{6\beta,8\beta}$. Confirmed by decoupling—see curves C and D, Fig. 1. ^{d} Estimated from pattern width (at 60 Mc./sec.) of 7-H and value of $J_{6\beta,7\beta}$. ^{e} Estimated from line width (at 60 Mc./sec.) of 6-H and value of $J_{6\alpha,7\beta}$. Confirmed by spin decoupling; see curves F and G, Fig. 1. ^{f} Determined by spin decoupling (at 100 Mc./sec.) of 4-H from 6-H; curve G, Fig. 1. ^{g} Estimated from pattern width (at 60 Mc./sec.) of 7-H and value of $J_{6\alpha,7\beta}$. Confirmed by spin decoupling; see curves F and H, Fig. 1.

apart in a rigid system, wherein the protons are in close proximity. The two isomeric methyl ethers, of $6\alpha,7\alpha$-dichloroestrone (Ia) and of $6\beta,7\alpha$-dichloroestrone (Ib),[4] gave n.m.r. spectra, Table I, which

Ia, R_1 = Cl, R_2 = H
b, R_1 = H, R_2 = Cl
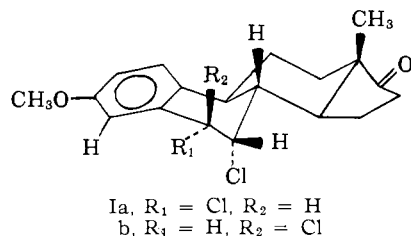
could be completely analyzed by means of multiple resonance spin–spin decoupling,[5] Fig. 1.[6] The coupling constants of the vicinal protons 6-H, 7-H, and 8-H were in the approximate range for *gauche* protons in a rigid system in the half-chair conformation of ring B.[7] Weak long-range couplings were observed between the aromatic (4-H) protons and the benzylic quasi-axial (6β-H) proton in Ia, and the corresponding quasi-equatorial (6α-H) proton in Ib. The most dramatic feature of the observed spectra was the unmistakable presence of the long-range coupling, $J = 1.8$ c.p.s., between the quasi-axial (6β-H) and axial (8β-H) protons of Ia, and the absence of a corresponding observ-

(4) Compound Ia, m.p. 164°, λ_{max}^{EtOH} 282 (2200), sh. 288 mμ (ϵ 2000); and Ib, m.p. 143°, λ_{max}^{EtOH} 289 mμ (ϵ 2400), were isolated as by-products of the oxofluorination (M. Neeman and Y. Osawa, *J. Am. Chem. Soc.*, **85**, 232 (1963)) of 6-dehydroestrone methyl ether. Correct analytical values were obtained for both compounds. The details of their synthesis and structure proof will be reported in a forthcoming paper.

(5) (a) R. Freeman and D. H. Whiffen, *Mol. Phys.*, **4**, 321 (1961). (b) We are grateful to Dr. E. A. Pier of Varian Associates, Palo Alto, California, for performing the spin decoupling experiments. (c) The first-order analysis is significant because $|\nu_i - \nu_j| \gg J_{ij}$ for all protons in the XABC system.

(6) The coupling constants reported represent absolute values of J. Their relative signs are as yet unknown.

(7) *Cf.* (a) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); (b) K. L. Williamson and W. S. Johnson, *J. Am. Chem. Soc.*, **83**, 4623 (1961), and F. J. Schmitz and W. S. Johnson, *Tetrahedron Letters*, 647 (1962); (c) J. W. Clark-Lewis and L. M. Jackman, *Proc. Chem. Soc.*, 165 (1961); (d) A. D. Cross, *J. Am. Chem. Soc.*, **84**, 3206 (1962); (e) E. D. Garbisch, *J. Org. Chem.*, **27**, 4249 (1962), estimated coupling constants in cyclohexenes of unknown degree of ring deformation. The effect of ring size and conformations of cycloalkenes on coupling constants was studied by (f) G. V. Smith and H. Kriloff, *J. Am. Chem. Soc.*, **85**, 2016 (1963), and (g) P. Laszlo and P. R. Schleyer, *ibid.*, **85**, 2017 (1963). Quantitative correlations of coupling constants and dihedral angles between vicinal protons are not of general applicability, but depend upon rigidity of the system as well as environmental effects, see ref. 7b; (h) R. U. Lemieux, J. D. Stevens, and R. R. Frazer, *Can. J. Chem.*, **40**, 1955 (1962), also in relation to the findings of F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 1053 (1962); (i) K. L. Williamson, *ibid.*, **85**, 516 (1963); (j) A. Nickon, M. A. Castle, R. Harada, C. E. Berkoff, and R. O. Williams, *ibid.*, **85**, 2185 (1963).
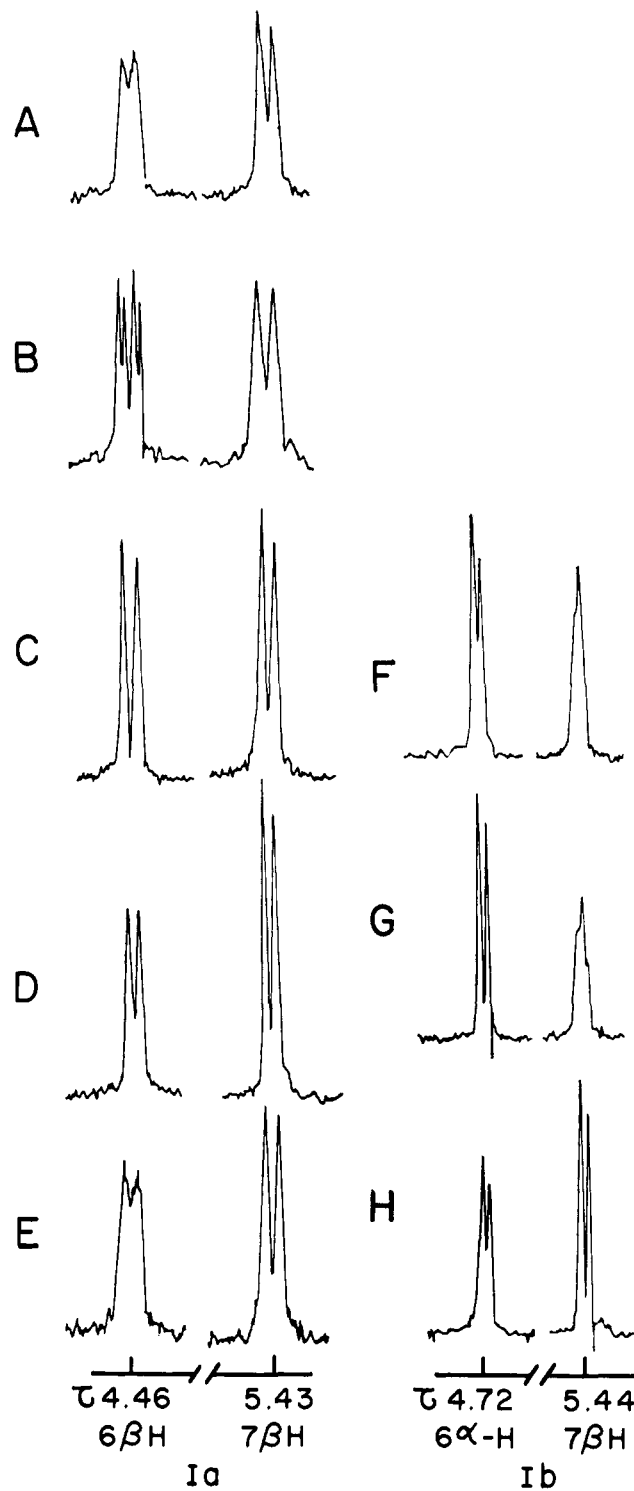

Fig. 1.—N.m.r. spectra of $6\alpha,7\alpha$-dichloroestrone methyl ether (Ia) (curves A–E) and of $6\beta,7\alpha$-dichloroestrone methyl ether (Ib) (curves F–H) in the 4.4–5.5 τ region (6-H and 7-H signals) at 100 Mc./sec. (CDCl$_3$ solution, TMS internal standard).

Curve	Decoupling irradiation, p.p.m.	Curve	Decoupling irradiation, p.p.m.
A	None	D	2.60 upfield (8-H)
B	1.56 downfield (4-H)	E	1.58 upfield (8-H)
C	1.54 downfield (4-H) and 2.58 upfield (8-H)	F	none
		G	1.52 downfield (4-H)
		H	2.03 upfield (8-H)

able coupling between the quasi-equatorial (6α-H) and axial (8β-H) protons of Ib. These findings define a

steric requirement for the novel type of long-range spin–spin coupling between 1,3-quasi-axial–axial protons.[8–10a]

(8) The steric requirement is defined primarily in terms of the juxtaposition of 6β-H and 8β-H, although the juxtaposition of the benzylic 6β-H and the aromatic system cannot be a priori disregarded as an element of the steric requirement. The weak, and sterically unspecific, couplings between both benzylic (6α-H and 6β-H) protons with the aromatic (4-H) proton could be regarded as evidence for the lack of strong σ–π interactions; this situation may be contrasted with the strong and sterically specific interactions between vinylic (4-H) and allylic (6β-H) protons, see ref. 1b and c. The juxtaposition of 6β-H and 8β-H is akin to the geometric arrangements, ref. 3d, Fig. 2 and 3, favorable for enhanced spin–spin coupling on the basis of overlap integrals of the C–H bond orbital wave functions calculated by Wiberg, et al., ref. 3d. Our findings therefore appear to accommodate the predictions from this treatment based on Fermi contact potential. In view of environmental effects, other than geometry, which may influence J_{HH} values, ref. 7, it is not yet warranted to consider this a conclusive experimental confirmation of the theory.

(9) The concept of "virtual long range spin–spin coupling," developed by Musher and Corey, ref. 3f, describes a "coupling" between nonvicinal protons, which occurs when, for example, protons B and C, in a closed linear 3-spin system, are strongly enough coupled so that proton A can "see" the spin states of C although it experiences no coupling strength from C, i.e., $J_{AC} = 0$. The XABC system described by us becomes a closed linear ABC system on decoupling of 4-H, Fig. 1 (B). As demonstrated by us, $J_{AC} \neq 0$, and this coupling is "real," not "virtual."

(10) (a) Supported by American Cancer Society Grant P-265 B; (b) Post-doctoral Fellow.

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An Electrochemical Method of Reducing Aromatic Compounds Selectively to Dihydro or Tetrahydro Products

Sir:

We hereby wish to report the development of the first successful electrochemical method of reducing aromatic compounds selectively to either dihydro or tetrahydro products.[1] A simple electrolytic cell shown in Fig. 1 was used.
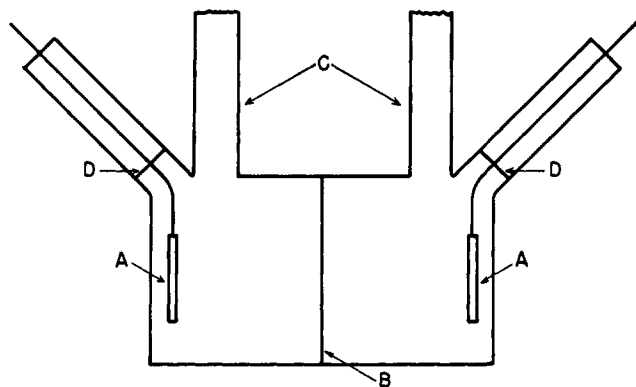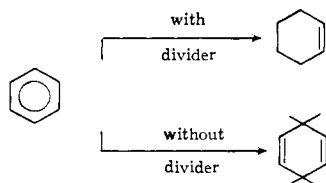

Fig 1.—A, platinum electrodes; B, asbestos; C, condensers; D, glass seal.

When aromatic compounds dissolved in methylamine were reduced in this cell without the asbestos divider (i.e., when the anode and cathode compartments were not separated) excellent conversions to dihydro products resulted. When the same aromatic compound

(1) A recent publication by H. W. Sternberg, R. Markby, and I. Wender, J. Electrochem. Soc., 110, 425 (1963), discloses the successful electrochemical reduction of benzene and tetralin. A mixture of reduction products was obtained and no increased selectivity was noted when an "anode compartment" was used.

TABLE I

ELECTROLYTIC REDUCTIONS OF VARIOUS AROMATIC HYDRO-
CARBONS IN METHYLAMINE–LITHIUM CHLORIDE SOLUTIONS
WITH AND WITHOUT CELL DIVIDER[a]

Aromatic[b]	Yield, %[c]	Alkyl-cyclo-hexenes, %	Dihydro-benzenes, %	Re-covered aromatic; %
Benzene[d]	49	4	95	1
Benzene[e]	49	100	. . .	. . .
Toluene[d]	64	5	94	. . .
Toluene[e]	44	86	. . .	14
Ethylbenzene[d]	73	4	93	. . .
Ethylbenzene[e]	63	96	. . .	4
Cumene[d]	82	6	78	13
Cumene[e]	75	89	. . .	11
t-Butylbenzene[d]	85	5	68	20
t-Butylbenzene[e]	81	53	. . .	47

[a] In those runs where the asbestos divider was used, 0.4 mole of LiCl was employed in each compartment. With no divider, 0.8 mole of LiCl was used. About 50,000 coulombs was passed through the solution in each case. The amperage varied between about 1.2 to 2 and the time of reduction was about 7–9 hr. in each case. [b] The amount of aromatic in every instance was 0.1 mole. [c] The yield in each case was calculated so as to take into account the amount of aromatic recovered. The per cent conversion would hence be lower. [d] Without asbestos cell divider. [e] With asbestos cell divider.

was reduced with the asbestos divider in place, equally excellent conversions to tetrahydro products resulted. Thus, benzene can be reduced to either cyclohexene or 1,4-dihydrobenzene by the simple device of carrying out the electrolytic reduction in the presence or absence of the cell divider.

Table I lists the results obtained when a representative series of aromatic hydrocarbons was reduced electrolytically both in the presence and absence of the cell divider. An electrolyte consisting of lithium chloride was used in each case.

All of the electrolyses were carried out under similar conditions. The preparation of 2,5-dihydroisopropylbenzene and the isopropylcyclohexenes which follows can be considered as typical.

An electrolysis cell (Fig. 1) 170 mm. in length by 100 mm. in diameter was fitted with two Dry Ice condensers, platinum electrodes (2 × 5 cm.), and an asbestos divider. Cumene (12 g., 0.1 mole) was placed in the cathode compartment. Lithium chloride (17 g., 0.4 mole) and 450 ml. of anhydrous methylamine were placed in each compartment. A total of 50,000 coulombs (2.0 amp.; 90 v.) was passed through the solution in 7 hr. The solvent was then allowed to evaporate and the mixture was hydrolyzed by the slow addition of water. After extraction with ether, drying, and removal of solvent, there was obtained 9.0 g. (75%) of product boiling at 149–153°. Analysis by v.p.c. (Aerograph, 14 ft. β,β' oxydipropionitrile column; 75°; 16 p.s.i. He) showed the presence of 89% isopropylcyclohexenes and 11% cumene.

When the same cell was used without the divider, 12 g. (0.1 mole) of cumene was reduced, using 34.0 g. (0.8 mole) of lithium chloride and 900 ml. of methylamine. Again, 50,000 coulombs (2.0 amp.; 85 v.) was passed through the mixture in 7 hr. Using the same work-up as described earlier, there was collected 9.8 g. (82%) of product boiling at 152–157°. Analysis by v.p.c. showed the presence of 6% isopropylcyclohexenes, 3% of an unidentified diene, 13% cumene, and 78% 2,5-dihydroisopropylbenzene.

When the reductions are carried out in the presence of the asbestos cell divider, the amine solution in the cathode compartment becomes deep blue in color. This color is highly reminiscent of the blue color ob-