[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

The Nitration of Monodeuterobenzene

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Nitration of benzene containing 91.5 mole % monodeuterobenzene gave nitrobenzene containing 74.9 mole % monodeuteronitrobenzene and *m*-dinitrobenzene containing 60.9 mole % monodeutero-*m*-dinitrobenzene. Since these are the concentrations expected if there is no hydrogen isotope effect, these studies confirm a previous report based on tracer studies that loss of a hydrogen ion cannot be a rate-influencing step in aromatic nitration. These values could not have resulted fortuitously from hydrogen exchange since nitration of normal benzene under identical conditions except in the presence of deuterosulfuric acid gave normal nitrobenzene and normal *m*-dinitrobenzene. A sample of the 91.5 mole % monodeuterobenzene lost 16.2% of its deuterium in less than an hour when heated at 50–60° in heterogeneous mixture with concentrated sulfuric acid. A sample of the 74.9 mole % monodeuteronitrobenzene lost none of its deuterium when treated under similar conditions in homogeneous mixture. This difference in ease of hydrogen exchange is in accord with the usual behavior of these molecules toward electrophilic aromatic substitution.

Introduction

Kinetic data have led Gillespie, Hughes, Ingold, Millen and Reed[2] to the conclusion that proton loss during aromatic nitration is kinetically insignificant. If the difference in electrical effects on the aromatic nucleus between the isotopes of hydrogen is negligible, then the extent of substitution of the nitro group for protium, deuterium or tritium must be directly proportional to the concentrations of these isotopic species present. Melander[3] has supplied confirmatory evidence in the case of the dinitration of benzene, toluene andb romobenzene, and in the mononitration of naphthalene, all containing the corresponding monotritio compounds in tracer amounts. Because of their great theoretical significance, we felt it desirable to extend Melander's observations under different conditions by studying the nitration of monodeuterobenzene. We hoped to prepare pure monodeuterobenzene since this would provide the ideal case where competition between protium and deuterium is entirely intramolecular and not also between molecules isotopically substituted differently. Since this result was not quite fully achieved, benzene containing 91.5 ± 1.7% monodeuterobenzene was used instead.

Experimental

Materials. Bromobenzene.—Eastman Kodak yellow label bromobenzene (1034 g.) was dried over calcium chloride and distilled through a Vigreux column. A forerun (303 g.) was discarded and a main fraction (597 g.), b.p. 143–145° (739 mm.), n^{20}_{D} 1.560, was collected.

Lithium Sand.—Partially oxidized lithium wire (16.8 g.) was cut into small pieces and heated above its melting-point in heavy mineral oil. The mixture was shaken thoroughly to pulverize the lithium, cooled, filtered and thoroughly washed with anhydrous ether.

Heavy Water.—"Norsk Hydro" deuterium oxide 99.75 g. D_2O/100 g., d^{20}_{4} 1.10514.

Phenyllithium—The lithium sand was suspended in 300 cc. of anhydrous ether. Over a period of three hours 157.3 g. (1.0 mole) of bromobenzene in 225 cc. of anhydrous ether was added dropwise with vigorous stirring. More lithium was added during the course of the addition in order to maintain a slight excess of lithium. After all the bromobenzene was added, the mixture was stirred and heated under reflux for 1.5 hours more.

Monodeuterobenzene.—Over a period of 1.5 hours 25.8 cc. (1.43 moles) of heavy water was added, with stirring, to the solution of phenyllithium. After all the heavy water was added, the mixture was stirred and heated under reflux for an additional hour. The precipitate was filtered off and the filtrate distilled through a Vigreux column, which removed most of the bromobenzene and all of the biphenyl. The lower boiling fractions were carefully fractionated through a 24-cm. column of Cannon protruded packing. After the ether had been removed, a forerun of 5.13 g., b.p. 78–78.5°, n^{25}_{D} 1.502, was discarded. The main run of 32.90 g. (41.6%) of monodeuterobenzene, b.p. 78.5°, n^{25}_{D} 1.498, was collected.

Anal. Calcd. for C_6H_5D: C, 91.08; H, 7.79. Calcd. for C_6H_6: C, 92.26; H, 7.74. Found: C, 90.70, 90.72; H, 8.05, 7.68.

An afterrun of 1.97 g., n^{25}_{D} 1.495, was discarded.

Nitric Acid.—"du Pont C.P. Reagent (Minimum 70.0%) Nitric Acid."

Sulfuric Acid.—"du Pont C.P. Reagent (Minimum 95.5%) Sulfuric Acid" (44.3 mole % SO_3 + 55.7 mole % H_2O).

Deuterosulfuric Acid.—To 56.1268 g. of "Baker C.P. Reagent (21.0% SO_3) Fuming Sulfuric Acid" (0.599 mole SO_3 + 0.452 mole H_2O) was added in portions 6.0359 g. (0.3006 mole D_2O + 0.0008 mole H_2O) of heavy water. Calculations indicate that the deuterosulfuric acid so prepared contained 44.3 mole % SO_3, 22.2 mole % D_2O and 33.5 mole % H_2O, the same acidity as the normal sulfuric acid.

Procedures. Nitration of Monodeuterobenzene.—Monodeuterobenzene (20.29 g., 0.256 mole) was nitrated with a mixture of 26.6 cc. (0.42 mole) of nitric acid and 30.4 cc. (0.54 mole) of sulfuric acid. The directions by Fieser[4] for the preparation and working up of nitrobenzene (with due allowance for the smaller quantities in this experiment) were followed scrupulously except that the monodeuterobenzene was added dropwise through an addition funnel. The crude product (28.7 g.) was dried over calcium chloride and distilled through a Claisen adapter containing a short length of Cannon protruded packing. A forerun of 0.78 g. (2.5%), b.p. 200–205°, was discarded. The main run of 19.53 g. (62.2%) of monodeuteronitrobenzene, b.p. 205–208.5°, n^{20}_{D} 1.5528, n^{25}_{D} 1.5511, was collected. An afterrun of 3.13 g. (10.0%), b.p. 210–265°, n^{25}_{D} 1.5583, was discarded. Upon crystallization from ethanol–water the distillation residue yielded 3.39 g. (7.8%) of crude monodeutero-*m*-dinitrobenzene, m.p. 86–90°, which upon recrystallization yielded 1.90 g. (4.4%) of pure product, m.p. 91–92°.

Nitration of Normal Benzene in Presence of Deuterosulfuric Acid.—Normal benzene (20.0 g., 0.256 mole) was nitrated with a mixture of 36.96 g. (0.411 mole) of nitric acid and 55.64 g. (0.537 mole SO_3) of deuterosulfuric acid. Calculations indicate that the hydrogen in the mixed acid contained 30.6 atom % deuterium. The procedure for the nitration of normal benzene and workup of the product was identical with the procedure for the nitration of monodeuterobenzene. A first forerun of 0.92 g. (2.9%), b.p. 204–206.5° (745 mm.), n^{25}_{D} 1.5493, and a second forerun of 1.33 g. (4.2%), b.p. 206.5–207° (745 mm.), n^{25}_{D} 1.5500, were

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[1] du Pont Postdoctoral Fellow 1951–1952.

[2] (a) R. J. Gillespie, E. D. Hughes, C. K. Ingold, D. J. Millen and R. I. Reed, *Nature*, **163**, 599 (1949); (b) E. D. Hughes, C. K. Ingold and R. I. Reed, *J. Chem. Soc.*, 2400 (1950).

[3] (a) L. Melander, *Acta Chem. Scand.*, **2**, 440 (1948); (b) L. Melander, *ibid.*, **3**, 95 (1949); (c) L. Melander, *Nature*, **163**, 599 (1949); (d) L. Melander, *Arkiv. Kemi*, **2**, 213 (1950).

[4] L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, Mass., 1941, p. 145.

discarded. The main run of 15.86 g. (50.3%) of nitrobenzene, b.p. 207–208.5° (745 mm.), $n^{25}\text{D}$ 1.5502, was collected. An afterrun of 5.60 g. (17.8%), b.p. 207–208.5° (745 mm.), $n^{25}\text{D}$ 1.5502, was discarded. The distillation residue was boiled with ether and filtered to remove insoluble charred material. The filtrate was dried with sodium sulfate, filtered, and the ether allowed to evaporate. The residue of 4.10 g. (9.5%) was crystallized from absolute ethanol and recrystallized from ethanol–water, yielding 1.73 g. (4.0%) of still slightly orange-colored crystals. After decolorization with charcoal and recrystallization from absolute ethanol *m*-dinitrobenzene, 1.12 g. (2.6%), m.p. 91–91.5°, was obtained.

Proton Exchange Test on Monodeuterobenzene.—Monodeuterobenzene (9.80 g., 0.124 mole) was treated with 20.3 cc. (0.36 mole) of sulfuric acid. The procedures used for the nitration of monodeuterobenzene and for working up the product (with due allowance for the smaller quantities in this experiment) were followed scrupulously. A fore-run of 0.09 g., b.p. up to 78° (737 mm.), and a second fore-run of 0.18 g., b.p. 78–78.5° (737 mm.), were discarded. The main run of 4.37 g. (44.6% recovery) of monodeuterobenzene, b.p. 78.5–78.7° (737 mm.), was collected. An afterrun of 0.05 g., was discarded.

Proton Exchange Test on Monodeuteronitrobenzene.—Monodeuteronitrobenzene (14.99 g., 0.121 mole) was treated with 14.7 cc. (0.26 mole) of sulfuric acid. The procedure used for the nitration of monodeuterobenzene was followed scrupulously. Unlike the mixture of monodeuterobenzene and sulfuric acid, the mixture of monodeuteronitrobenzene and sulfuric acid was completely homogeneous. After the exchange test was over, the homogeneous solution was diluted with 53 cc. of water, which caused the monodeuteronitrobenzene to separate. The recovered product was washed with 5 cc. of water, then with 32 cc. of 1.7% sodium hydroxide solution, and finally with 27 cc. of water. The product was dried over calcium chloride and distilled. A forerun of 0.80 g. (5.3%), b.p. 199–203°, $n^{25}\text{D}$ 1.5503, was discarded. A main run of 10.33 g. (69.0% recovery) of monodeuteronitrobenzene, b.p. 203–205°, $n^{25}\text{D}$ 1.5503, was collected.

Deuterium Analysis.—Procedures for the combustion of deuterated organic compounds to give deuterium-containing water, followed by reduction with hot zinc[5] or magnesium amalgam[6] to give a mixture of hydrogen and heavy hydrogen suitable for mass spectrometer analysis, have already been described. Our apparatus was very similar to that of Graff and Rittenberg,[5e] with the exceptions noted below: There was no Tube G. The receiver for combustion water consisted of a narrow tube running into a small centrifuge tube, which was equipped with a well-greased 10/18 standard taper joint to facilitate easy removal and interchanging of receivers. The reduction tube was a 12 mm. Pyrex tube 21 cm. in length, exclusive of the 10/30 standard taper joints at each end. The reduction tube was packed with 30-mesh zinc granules (previously treated with dilute hydrochloric acid, thoroughly washed with water, and dried *in vacuo*) for a distance slightly less than the 10.7 cm. within the reduction furnace. The zinc granules were held in place by a small plug of glass wool at the outlet end of the packing, but within the furnace. To the inlet end of the reduction tube was attached a U-shaped tube equipped with 10/30 standard taper joints to facilitate removal of the reduction tube. The water trap at the outlet end of the reduction tube was also equipped with 10/30 standard taper joints to facilitate removal. "Apiezon Grease N" provided vacuum tight seals, except in the warmest weather. The glass tubing used was 2-mm. capillary tubing.

Our experiences with the apparatus differed to no significant extent from those of Graff and Rittenberg.[5e] To avoid the source of error pointed out by other workers[5b,d] arising from fractionation due to differential rates of evaporation and diffusion, water samples were always reduced completely. The hydrogen from the first reduction of a new water sample was always discarded because of contamination by the previous sample arising from the "memory effect." In the event that the sample was somewhat different from the preceding sample in deuterium content, it was usually necessary to discard the hydrogen from the second sample also. Whenever possible, reductions were run in series in order of increasing deuterium content in order to minimize memory effects. Under such circumstances the hydrogen samples from the second, third and sometimes a fourth reduction were collected and submitted for mass spectrometer analysis. When the analysis from the second sample differed from the third in the direction expected from the memory effect, the result from the second sample was discarded. Otherwise, the results were averaged. In most cases the third reduction from the same water sample was free from significant memory effects. For the precise analyses of doubly distilled water a fresh zinc reduction tube was used in order to avoid trace residual amounts of deuterium from the previous reduction of high deuterium samples.

The mass spectrometer analyses for the mass 3/mass 2 ratio in the hydrogen samples were performed by John Saari under the direction of Professor A. O. C. Nier of the University of Minnesota Physics Department. The equation used to convert the mass 3/mass 2 ratio (r) obtained from mass spectrometer analysis to atom % deuterium is

$$\text{atom \% D} = \frac{100r}{2 + r} \quad {}^{5b}$$

This equation is derived from the assumption that the equilibrium constant for the reaction

$$H_2 + D_2 \rightleftharpoons 2HD$$

at the temperature of the zinc reduction (about 400°) is 4. The calculated value at 397° is reported to be 3.73.[7] Calculations are greatly simplified by the use of the approximate value 4 and no significant error is introduced below 2 atom % D, which includes most of the useful range in which the mass 3/mass 2 ratio corresponds to the HD/H_2 ratio.

Table I shows the results of analyses of the doubly distilled (conductivity) water available in this Laboratory. The value of 0.0151 atom % D corresponds to a ratio of H/D atoms of 6620 or a weight ratio of 1 part D_2O in 5960 parts H_2O. It agrees well with another mass spectrometer value of 0.0150 atom % D for distilled water,[5c] and with two of the other reported values for the natural abundance of deuterium: 0.0149 atom % D[8] and 0.0153 atom % D.[9] The series of heavy water solutions whose analyses are reported in Table II was prepared by successive gravimetric dilutions of heavy water with the sample of normal water whose analysis is reported in Table I. Agreement between calculated and found values appears satisfactory over the concentration range studied.

TABLE I

DEUTERIUM CONTENT OF DOUBLY DISTILLED NORMAL WATER

Run no.	Atom % D
2-18(2)	0.0154
2-18(3)	.0150
2-18(4)	.0146
2-20(1)	.0155
2-21(1)	.0152
2-21(2)	.0149
2-21(3)	.0152
Mean	0.0151 ± 0.0003[a]

[a] Standard deviation.

Since the deuterium content of our deutero-organic compounds far exceeded 2.5 atom % D, the maximum which

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[5] (a) D. B. Sprinson and D. Rittenberg, "U. S. Naval Med. Bull.," Supplement, p. 82, March–April, 1948; (b) R. B. Alfin-Slater, S. M. Rock and M. Swislocki, *Anal. Chem.*, **22**, 421 (1950); (c) P. R. Schloerb, B. J. Friis-Hansen, I. S. Edelman, A. K. Solomon and F. D. Moore, *J. Clin. Invest.*, **29**, 1296 (1950); (d) A. K. Solomon, I. S. Edelman and S. Soloway, *ibid.*, **29**, 1311 (1950); (e) J. Graff and D. Rittenberg, *Anal. Chem.*, **24**, 878 (1952).

[6] D. H. W. DenBoer and W. A. J. Borg, *Rec. trav. chim.*, **71**, 120 (1952).

[7] D. Rittenberg, W. Bleakney and H. C. Urey, *J. Chem. Phys.*, **2**, 48 (1934).

[8] Reference 5c quoting from R. J. Voskuyl, thesis, Harvard University, Cambridge, Mass., 1938.

[9] Recalculation by J. A. Swartout and M. Dole, THIS JOURNAL, **61**, 2025 (1939), of the result of N. F. Hall and T. O. Jones, *ibid.*, **58**, 1915 (1936).

Table II

Deuterium Content of Heavy Water Solutions

Atom % D Calcd.	Found[a]	
2.12	2.16	±0.01
1.066	1.088	± .002
0.541	0.543	± .003
.278	.281	± .001
.1465	.1434	± .0003
.0808	.0790	± .0009

[a] With standard deviation from the mean of the found values.

can be determined accurately with the mass spectrometer from the mass 3/mass 2 ratio, it was necessary to dilute the heavy hydrogen with normal hydrogen. With monodeuterobenzene this was done by diluting the water of combustion with normal water. With the monodeuteronitrobenzenes it was feared that the nitric acid, formed upon contact of nitrogen oxides with water, being a strong electrolyte, would concentrate in the combustion water and lead to erroneous weights for the water. Consequently, the monodeuteronitrobenzenes were diluted with pure normal nitrobenzene prior to combustion. The use of benzene as a diluent led to less reproducible values. In all calculations it has been assumed that the deuterium content of the hydrogen of normal bromobenzene and nitrobenzene is 0.0151 atom %, the same as normal water (see Table I), and this assumption appears justified.[10]

Results

Table III

Deuterium Content of Normal Benzene and its Nitration Products Formed in the Presence of Deuterosulfuric Acid

Compound	Atom % D[a]
Benzene	0.019 ± 0.002[b]
Nitrobenzene	.017 ± .002[b]
m-Dinitrobenzene	.020 ± .001[b]

[a] Contamination by trace residual amounts of deuterium from the previous reduction of high deuterium samples caused these values to be slightly higher than the normal isotope distribution (0.015 atom % D) found in distilled water. These residual traces are detectable only in samples of very low deuterium concentration. It is practically impossible to remove them without installing a fresh zinc reduction tube—an operation which was unnecessary here since absolute values were not required. [b] Standard deviation.

Table IV

Deuterium Content of Monodeuterobenzene

Combustion water, g.	Normal water, g.	Atom % D found	Mole % monodeuterobenzene above normal isotopic distribution
	Before proton exchange test		
0.0393	0.4821	1.132	90.4
.0307	.2549	1.599	88.3
.0327	.3698	1.220	91.7
.0295	.3569	1.186	93.6
.0386	.4285	1.265	92.2
.0383	.4461	1.212	92.3
.0434	.5257	1.170	92.3
		Mean	91.5 ± 1.7[a]
	After proton exchange test		
0.0261	0.3128	0.993	77.3
.0242	.2476	1.109	76.7
.0152	.1440	1.209	76.1
		Mean	76.7 ± 0.6[a]

[a] Standard deviation.

Table V

Deuterium Content of Monodeuteronitrobenzene

Monodeuteronitrobenzene, g.	Normal nitrobenzene, g.	Atom % D found	Mole % monodeuteronitrobenzene above normal isotopic distribution
	Before proton exchange test		
0.1090	1.0771	1.374	74.4
.1090	1.0771	1.399	75.7
.1090	1.0771	1.376	74.5
		Mean	74.9 ± 0.7[a]
	After proton exchange test		
0.1088	1.0254	1.408	73.0
.1055	1.0179	1.430	75.8
.1055	1.0179	1.424	75.4
.1037	1.0232	1.425	75.8
.1067	1.0035	1.498	77.6
		Mean	75.5 ± 1.6[a]

[a] Standard deviation.

Table VI

Deuterium Content of Monodeutero-*m*-dinitrobenzene

Monodeutero-*m*-dinitrobenzene, g.	Normal nitrobenzene, g.	Atom% D found	Mole % monodeutero-*m*-dinitrobenzene above normal isotopic distribution
0.1198	1.0930	0.964	63.1
.1198	1.0930	.923	60.4
.1198	1.0930	.905	59.2
		Mean	60.9 ± 2.0[a]

[a] Standard deviation.

Discussion

The nitration of normal benzene in the presence of the deuterosulfuric acid would have given nitrobenzene and *m*-dinitrobenzene containing hydrogen having 16.3 atom % deuterium if the deuterium had become randomly distributed between the hydrogen of the benzene and acid. Table III shows that the nitrobenzene and *m*-dinitrobenzene from this experiment contained no more deuterium (0.019 atom %) than normal benzene measured under the same conditions. Because of the normal hydrogen isotope effect, exchange of deuterium onto an aromatic nucleus would be expected to occur more readily than its replacement by hydrogen. Since the same acid concentration was used in the nitration of monodeuterobenzene, the possibility of loss of deuterium by exchange with the acid appears, therefore, to be excluded during nitration.

In another experiment monodeuterobenzene was subjected to the same conditions of time (less than one hour) and temperature (50–60°) as prevailed during the nitration. The acid strength, however, was substantially greater because the nitric acid was replaced by an equivalent amount of sulfuric acid, in addition to the same proportion of sulfuric acid as was used in the nitration. Furthermore, the sulfuric acid was not diluted by water of reaction, as was the case in the nitration reaction. The mole % monodeuterobenzene in the benzene recovered from this heterogeneous test reaction was 76.7 (Table IV), compared with an original value of 91.5, showing that 16.2% of the deuterium in the benzene had exchanged out. If the deuterium had become randomly distributed between the hydrogen

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[10] M. Dole, This Journal, **58**, 580 (1936).

of the benzene and sulfuric acid, the deuterium in the benzene would have been equivalent to 41 mole % monodeuterobenzene meaning that 55% of the deuterium in the benzene would have exchanged out. The reverse of this reaction, the deuteration of normal benzene with deuterosulfuric acid, has been studied by Ingold, Raisin and Wilson,[11] who found that this exchange was independent of sulfonation and could be made to occur even at room temperature, if given sufficient time. These workers found it impossible to cause deuteration to precede nitration of normal benzene with deuteronitric acid,[11c] and their report was confirmed by Melander,[3c,d] who found that no tritium was introduced into the aromatic nucleus during the dinitration of normal toluene with nitric and sulfuric acids containing a small amount of water labeled with tritium. These results and ours indicate that nitration is faster than hydrogen exchange and proceeds to the exclusion of the exchange reaction, yielding a product immune to exchange under the conditions used because of the deactivating effect of the nitro group. The relatively greater resistance of nitrobenzene to hydrogen exchange is rather strikingly shown by the proton exchange test (see Table V) where the nitrobenzene was completely dissolved in the sulfuric acid, whereas the mixture formed by benzene and sulfuric acid was heterogeneous. In this test, under the same conditions of time, temperature and proportion of sulfuric acid as were used in the test on monodeuterobenzene, the mole % monodeuteronitrobenzene in the nitrobenzene recovered was 75.5 ± 1.6, compared with an original value of 74.9 ± 0.7 mole %, indicating that none of the deuterium had exchanged out. If the deuterium had become randomly distributed between the hydrogen of the nitrobenzene and sulfuric acid, the deuterium in the nitrobenzene, would have been equivalent to 36 mole % monodeuteronitrobenzene.

TABLE VII

CALCULATED[a] DEUTERIUM CONTENT OF NITRATION PRODUCTS UNDER THREE ASSUMPTIONS

Assumption	Mole % monodeutero-nitrobenzene above normal isotopic distribution	Mole % monodeutero-*m*-dinitrobenzene above normal isotopic distribution
Exclusive substitution of H by NO_2	91.5	76.3
Indiscriminate substitution of H and D by NO_2	76.3	61.0
Exclusive substitution of D by NO_2	0	45.7

[a] From the mole % monodeuterobenzene above normal isotopic distribution present in the starting benzene (see Table IV). Calculations for the dinitro product are based on the fact that mononitration yields products formed by indiscriminate substitution of H and D by NO_2.

The 76.3 mole % monodeuteronitrobenzene calculated for indiscriminate substitution of H and D in monodeuterobenzene agrees fairly well with the found values of 74.9 ± 0.7 mole % monodeuteronitrobenzene before and 75.5 ± 1.6 mole % after the proton exchange test (see Table V). Similarly, the value of 61.0 mole % monodeutero-*m*-dinitrobenzene calculated for indiscriminate substitution of H and D in monodeuteronitrobenzene agrees with the 60.9 ± 2.0 mole % monodeutero-*m*-dinitrobenzene found (see Table VI). From these results we conclude that nitration of benzene and nitrobenzene containing a very large proportion of the corresponding monodeutero compounds occurs by substitution of protium or deuterium in direct proportion to the concentration of those isotopic species present. Within the limit of accuracy of our experiments there is no hydrogen isotope effect, as would have been expected if the loss of a proton or deuteron were a rate-influencing step in the nitration of benzene. Consequently, our results are in complete agreement with the conclusions of Melander.[3d]

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[11] (a) C. K. Ingold, C. G. Raisin and C. L. Wilson, *Nature*, **134**, 734 (1934); (b) *J. Chem. Soc.*, 915 (1936); (c) *ibid.*, 1637 (1936).