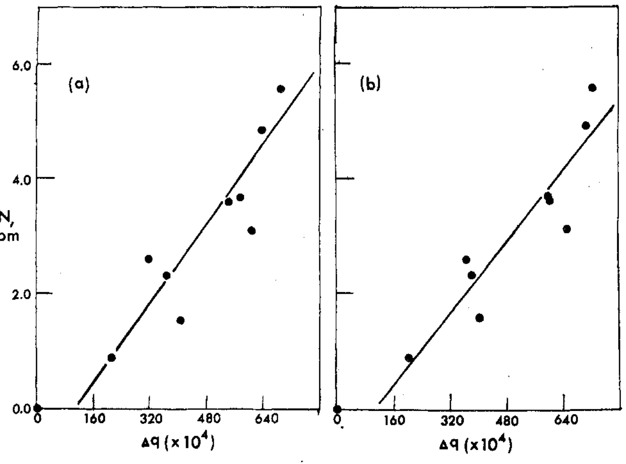

Figure 6. Plot of methylaniline chemical shifts *vs.* (a) excess total methyl electron densities and (b) excess methyl hydrogen electron densities. For (a) the values are the sum of the carbon and hydrogen electron densities of all the methyl groups, while for (b) only the hydrogen electron densities were taken. All values are given with respect to corresponding values in toluene. The least-squares lines (r = 0.924 and 0.939, respectively) were determined with all points included.

the methyl proton chemical shifts. This possibility is being explored.

It should be noted that the electron density at a given carbon of a disubstituted aniline is approximately the sum of the values at the corresponding carbons in the appropriate toluidine. This result is expected and indicates that there is no mutual electronic interaction between pairs of methyl groups.

It thus appears that even within the limitations of the INDO method and particularly the geometrical assumptions on which the calculations are based, the aniline nitrogen shifts depend on total electron density.

Acknowledgments. We are grateful to Professor David Beveridge for making the CNINDO program available to us and to Professor Joseph Dannenberg and Dr. Roderick Wasylishen for many enlightening discussions. This work was supported by a CUNY Faculty Research Award and by the Research Corporation. Funds for the nmr spectrometer were provided in part by National Science Foundation Instrumentation Grant No. GP-37025.

Registry No.—Aniline, 62-53-3.

References and Notes

(1) R. L. Lichter and J. D. Roberts, *Org. Magn. Resonance*, in press.
(2) T. Axenrod, P. S. Pregosin, M. J. Wieder, E. D. Becker, R. B. Bradley, and G. W. A. Milne, *J. Amer. Chem. Soc.*, **93**, 6536 (1971).
(3) R. L. Lichter and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 3200 (1971).
(4) R. A. Cooper, R. L. Lichter, and J. D. Roberts, *J. Amer. Chem. Soc.*, **95**, 3724 (1973).
(5) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.
(6) D. G. Lister and J. K. Tyler, *Chem. Commun.*, 152 (1966).
(7) W. J. Hehre, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **94**, 1496 (1972).
(8) G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Amer. Chem. Soc.*, **94**, 3089 (1972).
(9) (a) L. Paolillo and E. D. Becker, *J. Magn. Resonance*, **2**, 168 (1970); (b) M. Alei, Jr., A. E. Florin, and W. M. Litchman, *J. Amer. Chem. Soc.*, **92**, 4828 (1970).
(10) (a) W. F. Reynolds, I. R. Peat, M. H. Freedman, and J. R. Lyerla, Jr., *Can. J. Chem.*, **51**, 1857 (1973); (b) G. K. Hamer, I. R. Peat, and W. F. Reynolds, *ibid.*, **51**, 897 (1973); (c) O. Kajimoto and T. Fueno, *Tetrahedron Lett.*, 3329 (1972).
(11) (a) P. S. Pregosin, E. W. Randall, and A. I. White, *J. Chem. Soc., Perkin Trans. 2*, 513 (1972); (b) P. Hampson, A. Mathias, and R. Westhead, *J. Chem. Soc. B*, 397 (1971).
(12) R. T. C. Brownlee and R. W. Taft, *J. Amer. Chem. Soc.*, **92**, 7007 (1970).
(13) P. Lazzeretti and F. Taddei, *Org. Magn. Resonance*, **3**, 283 (1971).
(14) An independent check of the calculations for these compounds using a different origin for the coordinate system gave the same results. We thank Ms. Alice J. DiGioia for her able assistance.
(15) The correlation with 2s orbital density is improved if sterically perturbed compounds 2,3-, 3,4-, and/or 2,6-xylidine are excluded. Evidently the steric effect manifests itself *via* the more voluminous p orbitals.
(16) J. E. Bloor and D. L. Breen, *J. Phys. Chem.*, **72**, 716 (1968).
(17) L. Libit and R. Hoffmann, *J. Amer. Chem. Soc.*, **96**, 1370 (1974).

The Mechanism of Equilibration of *cis*- and *trans*-2,3-Dimethyl-2,3-dihydrobenzofurans by Sulfuric Acid-d_2. Isomerizations Initiated by Oxonium Ions[1]

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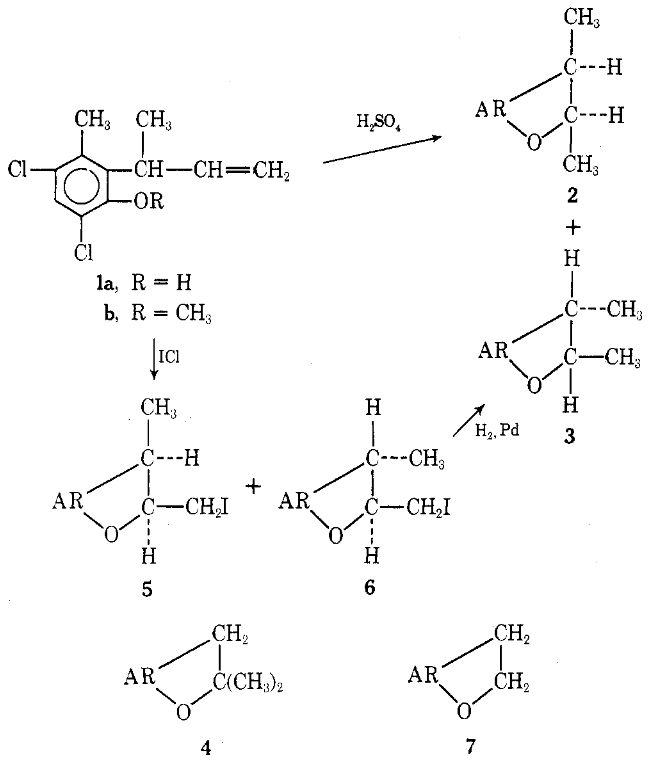
Treatment of pure *trans*-2,3,4-trimethyl-5,7-dichloro-2,3-dihydrobenzofuran (**3**) with D_2SO_4 at room temperature gives the cis and trans equilibrium mixture **2** and **3**; these show deuterium uptake at the free aromatic position, slow uptake at C-2 and C-3, slower uptake on the 2- and 3-methyl groups, and none at the aromatic methyl. There is also formed in small amount at room temperature, and in larger amounts at 42°, the 2,2,4-trimethyl compound **4**, the product of methyl rearrangement. This compound can exchange all of its hydrogens for deuterium. The compound without a 2-methyl group, 2,3-dihydro-4-methyl-5,7-dichlorobenzofuran (**7**), shows only exchange of the aromatic hydrogen with D_2SO_4. Compound **7** could not be synthesized by the usual cyclization reactions of β-bromo- or β-hydroxyethyl phenyl ethers, presumably because of the steric effect of the *o*-methyl group (in **8d** and **8e**); it was synthesized by a procedure involving the intermediate 2-allyl-3-methyl-4,6-dichlorophenol (**9b**). Mechanisms for the isomerizations, exchange, and methyl rearrangements are discussed. The changes due to D_2SO_4 and H_2SO_4 on **2**, **3**, **4**, and **7** were followed by using vpc, nmr, and mass spectral methods.

It was shown[2] earlier that cyclization of the phenol **1a** or the methyl ether **1b** by concentrated H_2SO_4 gave a mixture of the *cis*- and *trans*-2,3-dimethyl-2,3-dihydrobenzofurans **2** and **3**; a small amount of the product of methyl rearrangement, the 2,2-dimethyl compound **4** was also isolated and identified.[2]

It was found that isomer **2** was formed under kinetic control of the cyclization, but at longer reaction times, the thermodynamically more stable trans form **3** was favored, the equilibrium favoring the trans form at room temperature by about 4:1. Treatment of the phenolic ether **1b** with ICl gave mainly the *trans*-iodomethyl compound **6**, which



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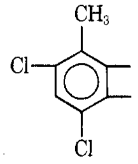


was related to the *trans*-2,3-dimethyl compound **3** by replacement of the iodine by hydrogen.

The basis for the configurational assignment for **2** and **3** has been previously described;[2,3] it included, in addition to other points conclusive in themselves, the determination of the coupling constants $J_{2\text{-H-}3\text{-H}}$ for **2** and **3**, and the calculation of coupling constants predicted from the Karplus equation and the 2-H-3-H dihedral angles, as determined from models.[4] It was found that in contrast to six-membered rings,[5] $J_{2\text{-H-}3\text{-H}}$ for the cis form **2** was larger than for the trans form **3**. This is mentioned here because there has been discussion about the applicability of the Karplus equation to assignment of configurations in 2,3-disubstituted 2,3-dihydrobenzofurans. It is now agreed, however, that $J_{2\text{-H-}3\text{-H}}$ is larger for cis protons than for trans protons in this five-membered ring, a conclusion supported by X-ray crystallography.[6]

The isomerization and equilibration of **2** and **3** by H_2SO_4, which was shown to be a true equilibration by starting from pure **2** or pure **3**, must involve carbonium ion formation by cleavage of the oxygen–carbon linkage of the hetero ring, or at least stretching this bond enough to allow interconversion of **2** and **3**; the methyl-rearranged product **4** must result from a carbonium ion.

The many interesting recent developments in carbonium ion chemistry[7] suggested a study of the equilibration of **2** and **3**, and the formation of **4**, by D_2SO_4, using vpc, nmr, and mass spectroscopy. The present paper reports the results of such a study.

The earlier results[2] with H_2SO_4 were first confirmed, starting with the pure trans compound **3**. Compound **3** was then treated[8] with concentrated D_2SO_4 at room temperature, and the products, as shown by vpc analyses, are indicated in Table I; the results were similar to those in H_2SO_4, although the amount of methyl-rearranged product, the 2,2-dimethyl compound **4**, was slightly smaller, and the trans/cis ratio was also slightly smaller for D_2SO_4 than for H_2SO_4. These differences are not very significant.

Table I
Action of D_2SO_4 at Room Temperature on Pure *trans*-2,3-Dihydro-2,3,4-trimethyl-5,7-dichlorobenzofuran (3)

Time, min	2,2-Dimethyl, product (4), %	*trans*-2,3-Dimethyl (3), %	*cis*-2,3-Dimethyl (2), %
0.5	1[a]	96	3
2	1	92	7
3	2	87	11
10	1	71	29
20	1	72	28
30	1	73	27

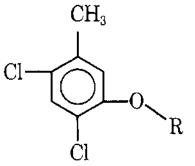
[a] These figures are too small to be very accurate.

Table II
Per Cent Hydrogen Remaining after D_2SO_4 Treatment of 3

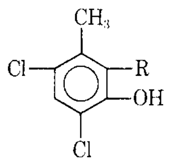
Time, min	Dihydrofuran CH_3	H at C-3	H at C-2	Aromatic H
0.5	100	90	69	79
2	100	100	73	76
3	100	100	75	66
10	96	41	35	26
20	96	22	16	11
30	97	23	23	12
Chemical shift, ppm	1.3–1.4	3.1	4.5	7.1

In Table II are given the amounts of hydrogen replacement by deuterium in the various positions for the entire sample, as a function of time. It is clear that the 2- and 3-methyl groups showed only a negligible exchange; that which occurred was undoubtedly due to the small amount of the 2,2-dimethyl compound present (see Tables I and II).

The hydrogen at C-2 exchanged somewhat more rapidly than the one at C-3, while the aromatic hydrogen exchanged most rapidly. Treatment of 2,4-chloro-5-methylphenol (**8a**) with D_2SO_4 gave only exchange of the aromatic hydrogens, and none with the methyl on the aromatic ring. There was no evidence for exchange of the aromatic methyl hydrogens with **3** and its transformation products (see below).



8a, R = H
b, R = C_2H_5
c, R = $CH_2CH{=}CH_2$
d, R = CH_2CH_2OH
e, R = CH_2CH_2Br



9a, R = $CH_2C(CH_3){=}CH_2$
b, R = $CH_2CH{=}CH_2$
c, R = $CH_2CH{=}CH_2$; OCH_3 for OH
d, R = CH_2COOH; OCH_3 for OH
e, R = CH_2CH_2OH; OCH_3 for OH

The results in Table II were confirmed and extended by mass spectral analysis of the 2,2-dimethyl (**4**), the *trans*-2,3-dimethyl (**3**), and the *cis*-2,3-dimethyl (**2**) compounds, which were separated in that order from a vpc column and analyzed by an LKB mass spectrometer for the molecular ions (Table III).

Table III shows that with the *trans*- and *cis*-2,3-dimethyl compounds, the deuterium uptake was limited at shorter

Table III
Per Cent Deuterium Content of Components of Mixture from D_2SO_4 and Pure Trans 3 by Mass Spectrometry

Time, min	Excess atoms D	2,2-Dimethyl (4)	*trans*-2,3-Dimethyl (3)	*cis*-2,3-Dimethyl (2)
0.5	0	0	94	47
	1	0	6	25
	2	79	0	24
	3	21	0	4
2.0	0	0	84	34
	1	0	16	27
	2	52	0	32
	3	48	0	7
3.0	0	0	74	23
	1	0	23	26
	2	39	3	39
	3	61	0	12
10.0	0	0	16	3
	1	11	40	10
	2	11	15	26
	3	9	24	49
	4	10	5	10
	5	15	0	2
	6	15	0	0
	7	12	0	0
	8	12	0	0
	9	5	0	0
20.0	0	0	6	1
	1	5	30	5
	2	3	18	17
	3	5	38	58
	4	6	8	15
	5	10	0	4
	6	14	0	0
	7	18	0	0
	8	24	0	0
	9	15	0	0
30.0	0	0	5	1
	1	5	28	5
	2	4	18	21
	3	11	42	56
	4	8	7	14
	5	9	0	3
	6	12	0	0
	7	17	0	0
	8	20	0	0
	9	14	0	0

times to three atoms, comprising the hydrogens at C-2 and C-3 of the hetero ring, and the aromatic proton. At longer times, there was evidently some limited exchange at the methyl groups on the hetero ring.

The 2,2-dimethyl compound **4**, although it was present in only small amounts in this mixture, exchanged much more rapidly up to a maximum of nine atoms (six methyl hydrogens on the hetero ring, the C-2, C-3, and the aromatic hydrogens). Treatment of the ethyl 2,4-dichloro-5-methylphenyl ether (**8b**) with D_2SO_4 caused exchange of both aromatic hydrogens, about 50% ether damage after 15 min, and almost complete cleavage of the ether after 12 hr. The aromatic proton ortho to the ether group was completely exchanged after 15 min, but the other proton was only partially exchanged during this interval.

Table IV
Action of H_2SO_4 on Pure *trans*-2,3-Dimethyl Compound (3) at 42°

Time, min	2,2-Dimethyl product (4), %	*trans*-2,3-Dimethyl (3), %	*cis*-2,3-Dimethyl (2), %
1		90	10
3	Trace	82	18
5	1	79	20
10	3	75	22
30	10	71	19
45	16	66	18
60	20	62	18

Table V
Per Cent Deuterium Uptake after Treatment of Pure 2,2,4-Trimethyl-2,3-dihydro-5,7-dichlorobenzofuran (4) with D_2SO_4 at Room Temperature

	Reaction time, min		
Excess atoms D	1	4	15
0	40	12	1
1	32	15	1
2	16	17	1
3	7	18	3
4	3	18	7
5	1	8	16
6	1	7	25
7		5	26
8		21	16
9			4

The data in Tables I–III raised some questions about the 2,2-dimethyl compound, which was formed in only small amounts and which exchanged all its hydrogens, except for the aromatic methyl groups, quite rapidly; once formed, however, it did not appear to re-form the *cis*- or *trans*-2,3-dimethyl compounds, because these did not show high deuterium content.

Varying the temperature of the equilibration answered some of these questions; at 19°, starting with the pure *trans*-2,3-dimethyl compound **3** and H_2SO_4 after 1 hr, there was little equilibration to the cis compound **2**, and no formation of the methyl rearranged product **4**. At 26°, the results of Table I were essentially confirmed. At 42°, however, the trans/cis equilibrium mixture of about 3.6:1 was established after 10 min, but the amount of the 2,2-dimethyl compound increased to about 20%. The results are given in Table IV. The action of H_2SO_4 on a mixture containing initially 84% of the *cis*- and 16% of the *trans*-2,3-dimethyl compounds **2** and **3**, at 26° and at 43°, gave results very similar to those in Table IV. Thus, the final mixture could be approached from both the cis and trans forms. The predominantly cis starting material in this run was prepared by a laborious separation (see Experimental Section) of the *cis*- and *trans*-2-iodomethyl compounds[2] **5** and **6**.

Experiment showed that the pure 2,2-dimethyl compound **4**, prepared as before,[2] was not converted by H_2SO_4 at room temperature for 30 min into any detectable amount of either of the 2,3-dimethyl compounds **2** and **3**. Therefore, the methyl-rearranged product **4** is formed from **2** or **3** irreversibly.

Treatment of the pure 2,2-dimethyl compound **4** with D_2SO_4 at room temperature showed the progressive uptake of deuterium (up to 9 D) given in Table V, in agreement with Table III, determined by mass spectrometric analysis. The nature of the hydrogens exchanged at various times, as determined by nmr, is given in Table VI, which, like Table V, shows that exchange has reached a steady state at about 15 min. At this point, there is enough H_2SO_4 present so that replacement of deuterium by hydrogen, or of hydrogen by hydrogen, becomes significant.

Table VI
Hydrogen Remaining after D_2SO_4 Treatment of 4, by Nmr Analysis

	Reaction time, min				
Functional group (ppm)	0	1	4	15	30
2,2-Dimethyl (1.5)	6	5.3	4.3	2.1	2.4
Aromatic methyl (2.1)	3	3	3	3	3
Furan C-3 hydrogens (2.9)	2	1.6	0.8	0.4	0.5
Aromatic hydrogen (7.0)	1	0.8	0.6	0.2	0.2

It was found that cyclization of the phenol **9a** to **4** by D_2SO_4, with a 30-min reaction period, gave about the same pattern of hydrogen exchange by deuterium as did the exposure of the preformed 2,2-dimethyl compound **4** to D_2SO_4 for the same period. This probably means that the cyclization of the phenol is rapid, and is followed by exchange with the cyclized product **4.**

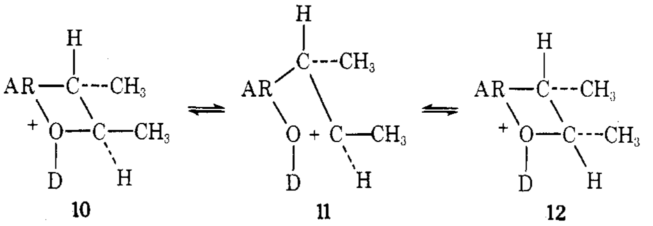
Acid cleavage of the O–C linkage in the hetero ring of **2** and **3** would lead to a secondary carbonium ion, and cleavage of **4** would give a tertiary carbonium ion. As mentioned above, the ethyl ether **8b** was cleaved to the free phenol. We, therefore examined the action of D_2SO_4 on the cyclic analog of the ethyl ether, the 2,3-dihydrobenzofuran **7,** which would give a primary carbonium ion on ring cleavage.

The synthesis of **7** proved to be more troublesome than expected; the cyclization of the β-hydroxyethyl ether **8d** and of the β-bromoethyl ether **8e** by a variety of reagents and conditions, which are reported to give 2,3-dihydrobenzofuran itself from the corresponding phenyl ether,[9] was unsuccessful. Compound **7** was finally obtained by preparation of the allyl ether **8c,** rearrangement to the allylphenol **9b,** methylation of the phenolic hydroxy to **9c,** oxidation of the allyl group to the acid **9d** with permanganate–periodate,[2,10] reduction to the primary alcohol **9e,** and cyclization of this to the dihydrobenzofuran **7** with HBr–AcOH.

A sample of **7,** after 10-min exposure to D_2SO_4, was purified and subjected to nmr and mass spectral analysis. The latter showed that 77% of the sample contained no deuterium, and 23% contained one deuterium. The nmr spectrum showed that the aromatic hydrogen was the only one replaced by deuterium, with 73% of the aromatic hydrogen remaining. There was no detectable amount of deuterium exchange for hydrogen on the hetero ring, and hence either no opening of the hetero ring by acid, or if there was, recyclization was faster than exchange. The experiments above on the ethyl ether **8b** would suggest that there was a reversible opening of the ring in **7,** but that recyclization was faster than exchange.

Discussion

The observations above support the following conclusions. Structure **10,** the deuterated oxonium trans form, could remain undeuterated on carbon by not reacting further, or it could open the ring to the carbonium ion **11,** which could recyclize to **10,** without change of configuration, more rapidly than any other process. The carbonium ion in **11** could also cyclize, with rotation around the single bond joining C-2 and C-3, so that the cis form **12** would be obtained, with a inversion of configuration at C-2. Neither

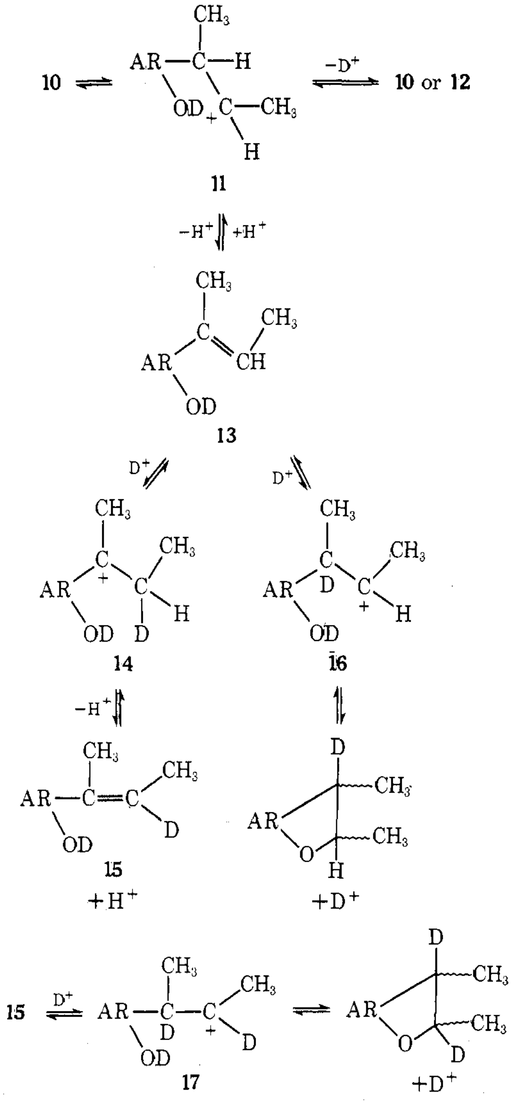


of these processes, as described, would lead to deuterium exchange.[11]

The data in Table III show, however, that there is much deuterium uptake in the cis form, which is generated from the pure transform, after 0.5 min, and that the deuterium content in the cis form increases rapidly with time, and increases (somewhat more slowly) in the trans form. This means that the simple scheme shown does not agree with the observations.

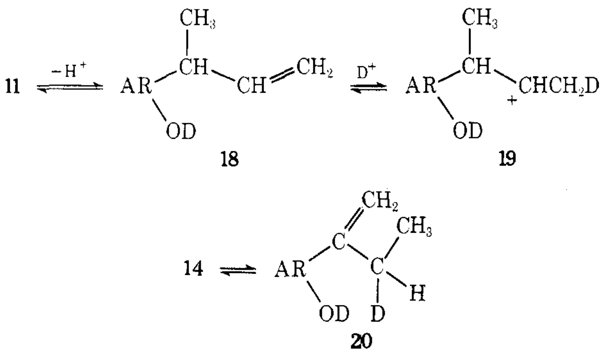
Table II shows that the aromatic hydrogen is exchanged at about the same rate as the C-2 and C-3 hydrogens, and hence the one deuterium uptake shown in Table III at short reaction times is not due solely to the aromatic hydrogen.[12]

The rapid rate of deuterium uptake at C-2 and C-3 must be due to processes involving **13** and the subsequent ions.

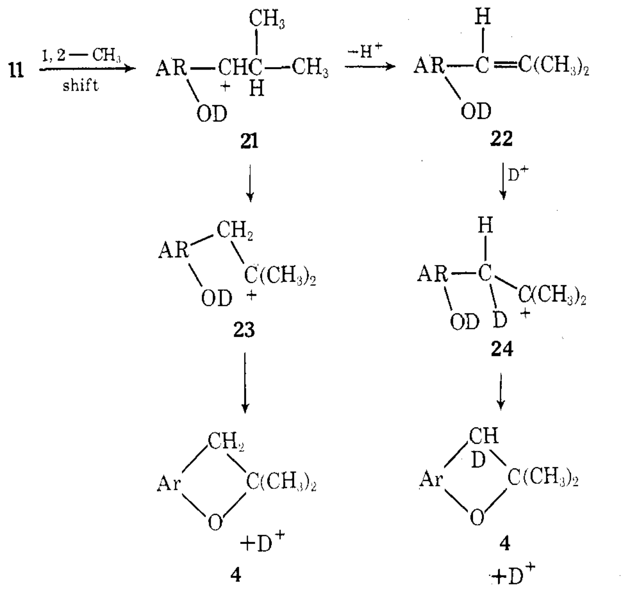


The relative slowness of exchange at the 2-methyl and 3-methyl indicates that the process **11** → **18** and **19** is not a competing one; the same is true for similar processes involving **20** which could incorporate deuterium at the 3-

methyl group, and then recyclize after several obvious stages.

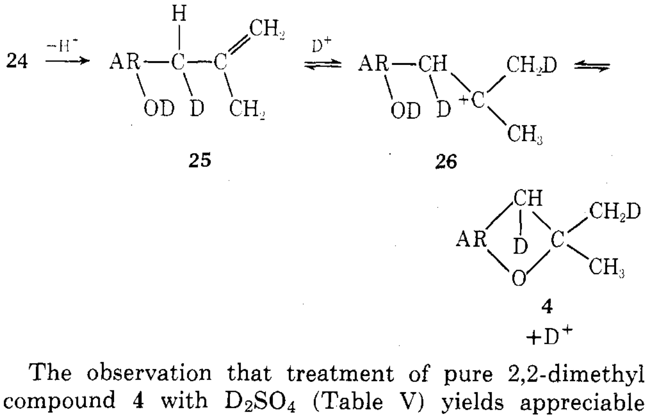


The *irreversible* shift of a methyl group to form the 2,2,4-trimethyl compound, *via* **21** and **23**, or *via* **22** and **24**, is to be expected from the greater stability of a tertiary carbonium ion compared to a secondary one.[13]



The pathway through **23** is rendered unlikely by the data in Table III, which show that at 0.5 min, the 2,2-dimethyl compound **4** contains 79% of doubly deuterated product, which could only come *via* **22** and **24**. The second deuterium would be in the aromatic nucleus.

The rate of exchange of the H at C-3 is roughly the same as that for the C-2 methyl groups (Table VI), so that the sequences **22** → **24** → **4** or **22** → **4** directly are indicated. Exchange of the methyl H in the 2,2-dimethyl compound may be readily explained *via* **24** → **25** → **26** → **4**, and a reversal of this process to complete the exchange of the methyl H's.



The observation that treatment of pure 2,2-dimethyl compound **4** with D_2SO_4 (Table V) yields appreciable amounts of undeuterated or monodeuterated material at 1 and 4 min is probably due to the fact that, if opened, the hetero ring can close without exchange. Furthermore, in this experiment, the isomers **2** and **3** were not present.

The carbonium ions written here differ from those usually suggested, in that the present ones contain a "solvent molecule" as part of the same molecule, in the shape of the -OD group; the rearrangement of the carbonium ion may thus be facilitated by the internal "solvation" by the adjacent -OD (or -OH) group, with the accompanying formation of the oxonium ion such as **10**. The relationships in the 2,2-dimethyl compound **4** are somewhat similar to those observed by Lansbury[14] in cyclization–rearrangement reactions.

The failure of **7** to exchange deuterium with D_2SO_4 undoubtedly reflects the much lower stability of a primary as compared to a secondary carbonium ion.[13] In a more strongly acidic solvent[15] such exchange would probably occur.

Experimental Section[16]

The D_2SO_4 used in initial experiments gave extensive decomposition of the dihydrobenzofuran **3**, whereas concentrated H_2SO_4 did not. This was eventually traced to an excess of SO_3 in this sample; titration of the sample with D_2O, using the formation of dense fumes as indicator,[17] gave a sample free[18] of SO_3.

trans-5,7-Dichloro-2,3-dihydro-2,3,4-trimethylbenzofuran (**3**) was made as described;[2] the cis compound **2**, consisting of 86% cis and 16% trans, was made from a mixture of the *cis*- and *trans*-iodomethyl compounds **5** and **6**,[2] by solution in petroleum ether and allowing solvent to evaporate slowly. Two types of crystals could be distinguished, which were separated by hand using forceps. The lower melting ones, after crystallization from the same solvent, melted at 61–64°. The pure *cis*-iodomethyl compound[2] melts at 64.5–65.5°. Replacement of the iodine by hydrogen[2] gave the cis-trans mixture of **2** and **3** described above, as determined by vpc.

Allyl 2,4-Dichloro-5-methylphenyl Ether (8c). To 17.7 g of 2,4-dichloro-5-methylphenol dissolved in 46 ml of dry acetone was added 14.5 g of anhydrous potassium carbonate, 100 mg of potassium iodide, and finally 12.1 g of allyl bromide. This solution was then heated at reflux with stirring for 24 hr. The product was worked up in the usual way, and the residual neutral oil (18.4 g) was analyzed without distillation.

Anal. Calcd for $C_{10}H_{10}OCl_2$: C, 55.33; H, 4.64. Found: C, 55.12; H, 4.61.

2-Allyl-3-methyl-4,6-dichlorophenol (9b). The allyl ether **8c** (18.4 g) was rearranged by refluxing for 12 hr in 40 ml of diethylaniline under N_2, and was worked up as described[2] for a similar case; the boiling point was 87–88° (0.01 mm).

Anal. Calcd for $C_{10}H_{10}Cl_2O$: C, 55.33; H, 4.64. Found: C, 55.10; H, 4.51.

This phenol was methylated to the corresponding **methyl ether 9c**, by refluxing with dimethyl sulfate and anhydrous potassium carbonate in acetone. The product, obtained in high yield by the usual work-up, boiled at 78–79° (0.01 mm).

Anal. Calcd for $C_{11}H_{12}OCl_2$: C, 57.17; H, 5.23. Found: C, 56.99; H, 5.24.

The corresponding **phenylacetic acid 9d** was prepared by oxidation with potassium permanganate–sodium metaperiodate in aqueous dixoane, as described for a similar compound.[2] The product (0.5 g from 2.5 g of starting material) was obtained pure by sublimation and melted at 135–137°.

Anal. Calcd for $C_{10}H_{10}O_3Cl_2$: C, 48.22; H, 4.05. Found: C, 48.41; H, 4.24.

3,5-Dichloro-2-methoxy-6-methylphenylethanol (9e). To 0.15 g of lithium aluminum hydride dissolved in 10 ml of anhydrous diethyl ether was added dropwise 75 ml of anhydrous ether which contained 2.5 g of 3,5-dichloro-2-methoxy-6-methylphenylacetic acid (**9d**). After the addition was complete, the reaction was allowed to stir at room temperature for 15 hr. Then water was added dropwise to the mixture, the solids were removed by filtration, and the ether solution was washed with water. The ether solution was then dried, followed by removal of the ether *in vacuo*. Distillation of the residue yielded 1 g of the product **9e**, bp 134–135° (0.75 mm).

Anal. Calcd for $C_{10}H_{12}O_2Cl_2$: C, 51.09; H, 5.14. Found: C, 51.34; H, 5.25.

Cyclization of 9e to 5,7-dichloro-4-methyl-2,3-dihydrobenzofuran (7). The ethanol derivative **9e** (0.5 g) was refluxed for 6 hr in a mixture of 12 ml of 48% hydrobromic acid and 20 ml of acetic acid. The hot solution was poured on ice and extracted with three 150-ml portions of ether. The combined ether extracts were washed with two portions of 10% sodium hydroxide and once with cold water. The ether portion was dried, the ether was removed *in vacuo,* and the residue was sublimed, yielding 0.25 g of product, mp 108–110°. All of the spectral properties, including the mass spectrum, were in agreement with the dihydrobenzofuran structure **7**.

Equilibrations in D_2SO_4 and H_2SO_4. These were carried out in general as described.[2] For D_2SO_4 runs, about a 1:4 (v/v) ratio of compound to acid was used. For H_2SO_4 runs at varying temperatures, about 1 g of compound per 12–15 ml of acid was used. After the desired time, the sample or an aliquot was quenched in water, extracted with ether, and dried, solvent was removed, and the sample was analyzed by vpc or mass spectrometry. The recovery of material in H_2SO_4 was around 75%, using the cis or trans compounds **2** and **3**. With the 2,2-dimethyl compound **4** and D_2SO_4, from 0.6 g of sample in 5 g of D_2SO_4, 42% of crystalline **4** was recovered, after two crystallizations from petroleum ether, using a Dry Ice–acetone bath.

For nmr determinations, a sample was weighed accurately and dissolved in a known volume of CCl_4.

The accuracy of the mass spectral deuterium determinations was about ±2%; the reproducibility of mass spectral runs on the same sample was ±1% or better. The nmr runs were reproducible on the same sample, and probably accurate within ±3%. The vpc analyses for the cis and trans compounds were accurate to ±2% or better; the methyl-rearranged product **4** was not completely resolved from the trans compound **3**, and for small amounts of **4** and large amounts of **3**, as in Table II, the accuracy of determining **4** is much lower. The vpc separations were done using 25% Ucon Polar columns.

Registry No.—**2,** 1876-14-8; **3,** 1876-13-7; **4,** 6834-35-1; **5,** 6834-34-0; **6,** 2030-78-6; **7,** 52259-73-1; **8c,** 1201-79-2; **9b,** 52259-74-2; **9c,** 52259-75-3; **9d,** 52259-76-4; **9e,** 52259-77-5; D_2SO_4, 13813-19-9; H_2SO_4, 7664-93-9; 2,4-dichloro-5-methylphenol, 1124-07-8; allyl bromide, 106-95-6.

References and Notes

(1) We are indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.
(2) D. P. Brust, D. S. Tarbell, S. M. Hecht, E. C. Hayward, and L. D. Colebrook, *J. Org. Chem.*, **31**, 2192 (1966).
(3) E. C. Hayward, D. S. Tarbell, and L. D. Colebrook, *J. Org. Chem.*, **33**, 399 (1968).
(4) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).
(5) R. V. Lemieux, *et al.*, *J. Amer. Chem. Soc.*, **79**, 1005 (1957), and later papers.
(6) L. H. Zalkow, E. Keinan, S. Steindel, A. R. Kalyanaraman, and A. Bertrand, *Tetrahedron Lett.*, 2873 (1972); M. P Mertes, L. J. Powers, and E. Shefter, *J. Org. Chem.*, **36**, 1805 (1971). For N-substituted 2,3-dimethylindolines, see F. A. L. Anet and J. M. Muchowski, *Chem. Ind.* (*London*), 81 (1963).
(7) For excellent summaries see (a) D. Bethell and V. Gold, "Carbonium Ions," Academic Press, New York, N. Y. 1967; (b) D. M. Brouner and H. Hogeveen, *Progr. Phys. Org. Chem.*, **7**, 179 (1972); (c) G. A. Olah, *Angew. Chem., Int. Ed. Engl.*, **12**, 173 (1973). *Cf.* also R. S. Schwartz, H. Yokokawa, and E. W. Graham, *J. Amer. Chem. Soc.*, **94**, 1247 (1972).
(8) For complications due to the presence of excess SO_3 in some samples of D_2SO_4, see Experimental Section.
(9) R. E. Rindfusz, P. M. Ginnings, and V. L. Harnack, *J. Amer. Chem. Soc.*, **41**, 665 (1919); **42**, 157 (1920).
(10) R. V. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701 (1955).
(11) It has been shown that carbonium ions themselves do not exchange deuterium but must first form the corresponding ethylenic linkage (by loss of proton) which can then add a deuteron from solvent: J. S. Coe and V. Gold, *J. Chem. Soc.*, 4185 (1960); V. Gold and R. S. Satchell, *ibid.*, 1930 (1963).
(12) *Cf.* C. Eaborn and G. J. Wright, *J. Chem. Soc. B*, 2262 (1971); P. Beak and R. N. Watson, *Tetrahedron*, **27**, 953 (1971), and references cited therein.
(13) Reference 7b, p 204.
(14) P. T. Lansbury and F. F. Hilfiker, *Chem. Commun.*, 619 (1969); P. T. Lansbury, *Accounts Chem. Res.*, **5**, 313 (1972).
(15) G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **90**, 933 (1968); M. Saunders and P. Vogel, *ibid.*, **93**, 2559 (1971).
(16) Elemental analyses were by Galbraith Laboratories. Mass spectra were obtained on an LKB mass spectrometer; vpc analyses were done on a Varian Aerograph 90-P instrument, and nmr spectra were determined in CCl_4 solution, using a Varian A-60 or a Jeolco 100 spectrometer. All melting points and boiling points are uncorrected. We are indebted to Dr. James R. Fehlner for assistance with the mass spectral and nmr determinations.
(17) R. G. Parker, *J. Soc. Chem. Ind.*, **36**, 692 (1917).
(18) This was worked out by Professor S. M. Hecht, of the Department of Chemistry at Massachusetts Institute of Technology, then an undergraduate at the University of Rochester.

Synthesis and Dehydrogenation of α-(9-Acridanyl)acetonitriles

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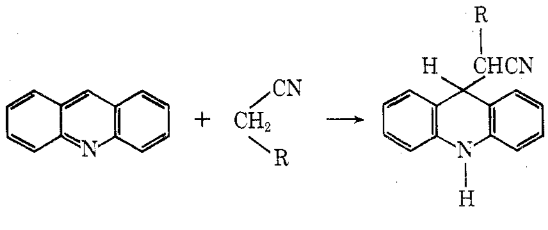
Four α-(9-acridanyl)acetonitriles [9-($C_{13}H_{10}N$)CRR′CN] were synthesized by the 9,10 addition of the anions (prepared using sodium amide) of the nitriles RR′HCCN (R = R′ = H; R = H, R′ = CH_3; R = CH_3, R′ = CH_3; and R = H, R′ = C_6H_5) to acridine. Two of these products (R = R′ = H and R = H, R′ = C_6H_5) were dehydrogenated to give exclusively the corresponding 9-cyanomethyleneacridans and a third (R = H, R′ = CH_3) was dehydrogenated to give a mixture α-(9-acridinyl)propionitrile (major product) and α-cyano-α-methyl-9-methyleneacridan (minor product). The fourth compound (R = R′ = CH_3) could not be dehydrogenated apparently for steric reasons.

Kröhnke and Honig[1] found that very active methylene compounds undergo noncatalytic 9,10 addition to acridine to give 9 substituted acridans. Since several years ago[2] we effected the 9,10 addition of sodio ketones to acridine to give α-(9-acridanyl) ketones which on dehydrogenation gave α-(9-acridanyl) ketones, it was decided to extend this work to the synthesis of α-(9-acridanyl)acetonitriles, **2.** The sodium derivatives of acetonitrile (R = R′ = H), propionitrile (R = H,R′ = CH_3), isobutyronitrile (R = R′ = CH_3), and phenylacetonitrile (R = H, R′ = C_6H_5) added to acridine to give 78.5%, 76.5%, 49.5%, and 87.0% yield of the corresponding acridanylacetonitriles, **2.** Phenylacetonitrile, the most reactive of the nitriles, failed to react under Kröhnke and Honig's noncatalytic conditions.



In all but one case, the only reaction products isolated were the α-(9-acridanyl)acetonitriles. With acetonitrile, in addition to 9-cyanomethylacridan (78.5%), there was obtained 10% of the dehydrogenated compound α-cyano-9-