TABLE III

CONDITIONS FOR GAS CHROMATOGRAPHIC ANALYSIS

Ether	Concn. of stock soln., vol. %	Column[a] packing	Column temp., °C.	Flow rate, ml./min.
Dimethyl	1	P	44	74
Methyl ethyl	2	T	62	60
Methyl *i*-propyl	3	T	54	95
Methyl *n*-propyl	2	T	60	60
Diethyl	2[c]	T	59	70
Diethyl[b]	2	T	62	70
Di-*n*-propyl	5	B	62	100
Di-*i*-propyl	2	A	74	90
Methyl *t*-butyl	2	A	82	100
Methyl *n*-butyl	2	A	76	110
Ethyl *t*-butyl	4	A	74	100
Ethyl *n*-butyl	5	B	67	92
Di-*n*-butyl	2	T	90	80
Anisole	3	A	120	76

[a] Burrell Corporation packings used as follows: A, Apiezon L on firebrick; B, β,β'-oxydipropionitrile on Celite; P, polyethylene glycol on Celite; T, Tween on Celite. [b] Solvent was carbon tetrachloride in this case. Cyclohexane used as extraction solvent in all other cases except anisole for which isoöctane was used (see previous paper). [c] Sample volume in this case was 10 μl. In all other cases 50 μl. was used.

confirmed by comparison of boiling point and refractive index with literature values and by infrared spectrum. A final check was made for impurities by gas chromatography.

Methyl ethyl ether was prepared by the action of 40 g. (0.73 mole) of sodium methoxide on 114 g. (0.73 mole) of ethyl iodide in 200 ml. of methyl alcohol as solvent.[52] The highly volatile product was distilled through a reflux condenser and collected by means of a Dry Ice condenser. Fractional distillation gave a portion boiling between 10–11°. The yield was 73%.

Methyl isopropyl ether was made by the procedure of Wirth, Jackson and Griffiths.[53]

The acids and solvents for distribution studies were prepared as described in the previous paper in this series.

Procedure.—The method has been described in the previous paper in this series.[4] Details of the gas chromatography for the compounds are presented in Table III.

Dimethyl ether is a gas at room temperature, the 1% solution was approximated in this case by bubbling the ether into chilled solvent until the volume increased by 1%.

Data for a typical series of extraction experiments with methyl ethyl ether are presented in Table IV.

TABLE IV

SOLVENT EXTRACTION OF METHYL ETHYL ETHER FROM CYCLOHEXANE AT 20°

% H_2SO_4	H_0	D	$\log \frac{D}{K_D' - D}$	pK_a
39.70	−2.39	1.622	1.849	−4.24
43.54	−2.74	1.469	0.922	−3.66
46.82	−3.06	1.367	.692	−3.75
48.84	−3.26	1.150	.366	−3.63
49.92	−3.37	1.005	.196	−3.57
53.73	−3.79	0.964	.149	−3.94
56.71	−4.11	.622	− .215	−3.89
57.44	−4.19	.465	− .404	−3.79
60.30	−4.51	.415	− .472	−4.04
62.13	−4.58	.298	− .656	−3.92

Acknowledgment.—It is a pleasure to acknowledge the encouragement and help of Professor Paul D. Bartlett who originally stimulated E. M. A. to work in this area. We are also grateful for valuable discussions with Professors Robert W. Taft, Jr., Norman Deno and Dr. Henry K. Hall, Jr. Mr. John Anderson performed the solvent extraction study on phenol.

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(52) D. McIntosh, *J. Am. Chem. Soc.*, **30**, 1098 (1908).

(53) H. E. Wirth, M. J. Jackson and H. W. Griffiths, *J. Phys. Chem.*, **62**, 871 (1958).

[CONTRIBUTION NO. 1112 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, PITTSBURGH 13, PENNA.]

Base Strengths of Some Saturated Cyclic Ethers in Aqueous Sulfuric Acid[1,2]

BY EDWARD M. ARNETT AND CHING YONG WU[3]

RECEIVED SEPTEMBER 7, 1961

The pK_a's of the oxonium ions of eight cyclic ethers have been determined by the solvent extraction–g.l.c. technique and found to follow the same order of basicity as was previously determined for the same ethers against six other acidic systems. The saturated cyclic ethers are more basic than their open chain analogs and steric hindrance to solvation is of much less importance than in acyclic compounds. A reverse I-strain order is found in the series: hexamethylene oxide $\geq$ tetrahydrofuran > tetrahydropyran, and also appears to obtain for the analogous imines. This cannot be explained by the usual polar or steric factors. An interpretation is advanced in terms of electron-correlation forces in the free base which lead to relief of non-bonded interactions upon protonation. When compared to the position of morpholine on the scale of basicities of saturated amines, dioxane is surprisingly basic. An explanation for this anomaly is presented.

In previous papers in this series we have evaluated the effect of changing structure on the basicities of aromatic[4] and acyclic saturated[5,6] ethers. In this article we shall present our results for the pK_a's of the oxonium ions of cyclic saturated ethers in aqueous sulfuric acid and interpret them in terms of polar, steric and solvation factors by comparison with basicities of the same ethers against non-aqueous acidic systems and with amine analogs. In doing this we shall make the usual assumption of the physical organic chemist, that modest changes in free energy of ionization may be understood in simple structural terms.

Cyclic ethers offer a distinct advantage over

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(1) Stereoelectronic Effects in Organic Bases, VIII; previous paper in this series, ref. 6.

(2) This investigation was supported by a Public Health Service research grant (A-3643 B.B.C.) from the National Institute of Arthritis Metabolic Diseases. The Perkin-Elmer 21 spectrophotometer used in conjunction with this work was purchased with the aid of the National Science Foundation. We wish to express our gratitude for this help.

(3) Most of the work presented here is taken from the thesis of Ching Yong Wu submitted to the Department of Chemistry of the University of Pittsburgh in March, 1961, as partial fulfillment of the requirements for the Ph.D. degree.

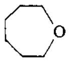
(4) E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **82**, 5660 (1960).

(5) E. M. Arnett and C. Y. Wu, *ibid.*, **82**, 4999 (1960).

(6) E. M. Arnett and C. Y. Wu, *ibid.*, **84**, 1680 (1962).

TABLE I

COMPARISON OF BASICITIES OF CYCLIC ETHERS AGAINST VARIOUS ACIDS

	Ether	pK_a this study	$\Delta\nu_{CH_3OD}$, cm.$^{-1}$	BF_3, kcal./mole	I_2,[a] kcal./mole	HCl[b] Henry's law constant	HCl,[c] sol. moles/mole	$CHCl_3$,[d] cal./mole
1		−2.02	122[e]					
2	Tetrahydrofuran	−2.08	117[f]	3.15[g]	1.70	2100	1.38	750
3	2,5-Dimethyltetrahydrofuran *cis*	−2.44						
4	*trans*	−2.65		2.88[g]				
5	2-Methyltetrahydrofuran	−2.65		2.76[g]	1.84			
6	Tetrahydropyran	−2.79	115[f]	2.51[g]	1.66	2600		600
7	7-Oxabicyclo[2.2.1]heptane	−2.80						
8	Dioxane	−3.22 (−2.92)[h]	111[f]		1.3	7500	1.046	
9	$CH_3OCH_2CH_2OCH_3$	−3.27 (2.97)[h]						
10	$C_2H_5OC_2H_5$	−3.59	96[f]	0.67[i]	1.12	4000	0.892	650
11	CH_3OCH_3	3.83		1.31[i]				

[a] ΔF^0_{298} for iodine–ether complex, ref. 9. [b] Ref. 15. [c] Ref. 14. [d] Heat of mixing with chloroform per mole of solution, ref. 10. [e] Determined by C. Y. Wu, this study. [f] Ref. 10. [g] Ref. 11. [h] Parenthesized figure is observed value; unparenthesized value is observed value corrected for symmetry factor for dibasic acids.[16] [i] Ref. 8.

their acyclic analogs in that their shapes are more predictable and rigid so that steric factors should be easier to analyze. Because of this hoped-for clarity of interpretation, the basicities of the cyclic ethers against a number of acid systems have been subjected to scrutiny by several groups of workers[7–15] and more data are available for comparison here than for the straight chain ethers.

Results and Discussion

I-Strain Series.—In Table I the pK_a's of cyclic ether oxonium ions in aqueous acid are compared with various other measures of basicity for the same compounds. It is at once striking that despite the widely different natures of the acidic systems, essentially the same order of basicity is always found for the cyclic ethers. In fact when the pK''s are plotted against the other measures of basicity for the same compounds linear correlations are generally produced. This is a very different situation from that encountered for the acyclic analogs of these ethers as described in the previous paper in this series[6] and is exactly what would be expected if F-strain to solvation were an important factor in the acyclic series but were of less influence in the unsubstituted cyclic ethers.

It is also to be noted that the cyclic ethers are in general five to ten times more basic than the simple acyclic ones. Tetrahydrofuran especially is found to be very basic in all systems, a fact which probably explains its superiority over other common ethers as a solvent for organometallic systems. The high basicity of tetrahydrofuran relative to acyclic compounds is clearly not due alone to a reduction in either F- or B-strain since it is sixty-three times more basic than dimethyl ether, although within experimental error both have the same COC bond angle of 111°.[17]

Comparison or tetrahydrofuran with tetrahydropyran and hexamethylene oxide shows that powerful internal forces are at work within the rings and that this part of the series is the reverse of the I-strain order which has been observed in a number of other reactions of five, six and seven-membered ring compounds.[18,19] (Unfortunately, the smaller ring ethers are too sensitive to aqueous acid to permit study by our method.)

We may dismiss polar factors from consideration here since their effects should be small and would increase in the order $5 < 6 < 7$. Likewise steric hindrance (F-strain) to solvation should be small and steadily increasing through the three ethers under consideration. It thus appears likely that the cause of the erratic order here is differences in conformational factors.

Brown attributes the I-strain order in "common"[18] rings to the relatively high bond opposition forces in the five- and seven-membered rings compared to the six-membered rings where relief of strain through staggering is possible. Although his arguments have been mainly developed for the reactions of substituted cycloalkane rings, they may be applied to the case in hand. Cass, Fletcher, Mortimer, Springall and White[20] have shown recently from heats of combustion that tetrahydrofuran is less stable by 2.9 kcal. than is tetrahydropyran. If the difference in basicity may be laid to this greater strain in the free base, it means that more strain is relieved by protonating tetrahydrofuran than tetrahydropyran. Many reactions of the cycloalkane derivatives of the common rings which give the I-strain order can be explained quite simply in terms of greater relief of non-bond-

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(7) H. C. Brown and R. M. Adams, *J. Am. Chem. Soc.*, **64**, 2557 (1942).

(8) D. E. McLaughlin, M. Tamres and S. Searles, Jr., *ibid.*, **82**, 5621 (1960).

(9) M. Brandon, M. Tamres and S. Searles, Jr., *ibid.*, **82**, 2129 (1960).

(10) S. Searles, Jr., and M. Tamres, *ibid.*, **73**, 3704 (1951).

(11) D. E. McLaughlin, M. Tamres, S. Searles, Jr., and S. Nukina, *J. Inorg. Nucl. Chem.*, **17**, 112 (1961).

(12) H. H. Sisler and P. E. Perkins, *J. Am. Chem. Soc.*, **78**, 1135 (1956), and previous papers.

(13) F. G. A. Stone, *Chem. Revs.*, **58**, 101 (1958).

(14) W. Gerrard and E. D. Macklen, *ibid.*, **59**, 1105 (1959).

(15) W. Strohmeier and A. Echte, *Z. Elektrochem.*, **61**, 549 (1957).

(16) S. W. Benson, *J. Am. Chem. Soc.*, **80**, 5151 (1958).

(17) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, Appendix.

(18) H. C. Brown, R. S. Fletcher and R. B. Johannesen, *J. Am. Chem. Soc.*, **73**, 212 (1951); **72**, 2926 (1950).

(19) For reviews of this topic see H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

(20) R. C. Cass, S. E. Fletcher, C. T. Mortimer, H. D. Springall and T. R. White, *ibid.*, 1406 (1958).

ing interactions when five- and seven-membered rings *lose* a group from the ring than when a six-membered ring does.[18,19] Clearly all that is necessary to bring our results into harmony with this reasonable picture is to explain why attachment of a proton to the cyclic ether oxygen leads to a decrease in ring strain rather than an increase. As will be shown below, the same anti-I-strain order of basicity probably also holds for the cyclic imines and hence requires a similar interpretation.

We suggest that a reasonable explanation may be found by employing a point of view toward molecular structure based on the effects of electron correlation.[21]

If one considers that the oxygen atom has sp^3-hybridization in the ethers (this is supported by the nearly tetrahedral angle found in these compounds), there is considerable repulsion between the non-bonded electron pairs on the oxygen and the electrons engaged in bonding the hydrogens to the nearby carbons. From this view a free electron pair behaves sterically like a medium-sized group. Upon coördination with a proton, the repulsion of a lone pair for nearby bonding pairs will be considerably reduced and this reduction will be greater for tetrahydrofuran (whose unshared electrons are constrained to orbitals that are eclipsed by the nearby bonds to hydrogen) than for tetrahydropyran where the orbitals and the nearby bonds are staggered. Hexamethylene oxide has lost the perfect staggering of the six-membered ring and its high basicity arises again from non-bonded repulsions in the free base.

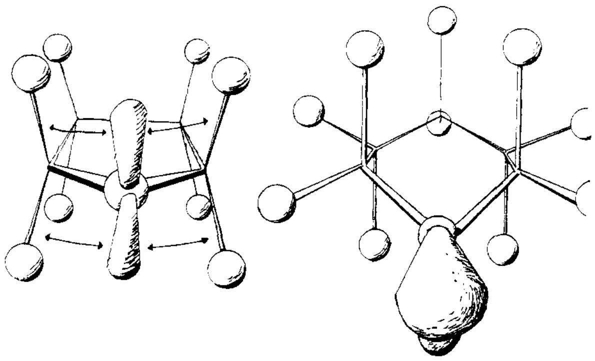

Fig. 1.

The electron correlation factor may also be used to explain the high sensitivity to steric effects of the basicities of ethers relative to amines. Since ethers have two unshared electron pairs exerting repulsions on neighboring bonding pairs rather than the single unshared pair of the amines, we might expect the alcohols and ethers to have greater inherent resistance to crowding than their nitrogen base analogs.

To our knowledge there is only one report in the literature in which the five; six- and seven-membered ring imines have been examined by the same authors at the same time and under the same conditions. Baddeley, Chadwick and Taylor[22] found that in 50% ethanol piperidine is considerably less basic than are either pyrrolidine or hexamethylene imine. They also observe the same order for the N-methyl substituted imines under the same conditions.[23] This suggests that the cyclic imines are also controlled by the same factors as influence basicities of the cyclic ethers.

Substituted Rings.—McLaughlin, Tamres, Searles and Nukina[11] found that 2,5-dimethyltetrahydrofuran was intermediate in basicity between tetrahydrofuran and 2-methyltetrahydrofuran, which they attributed to a gain of the inductive effect over F-strain. Their method of preparation by hydrogenation probably produced the *cis* compound. We prepared the 2,5-dimethyl compound by cyclization of hexane-2,5-diol with acid and obtained a material which upon gas chromatography gave two peaks close together and of equal size. These presumably correspond to the *cis* and *trans* isomers and we have determined their basicities by extraction without separating them (see Experimental). The superior basicity of the *cis* compound over the *trans* may be rationalized as a manifestation of the higher energy of the former if part of the strain is due to repulsions between bonding and non-bonding electrons such as we have invoked for the I-strain series above.

In contrast to the above results for aqueous acid or boron trifluoride as acid, Sisler and Perkins[12] have found that against dinitrogen tetroxide 2,5-dimethyl- and 2-methyltetrahydrofuran are more basic than tetrahydrofuran itself, which is in turn more basic than tetrahydropyran.

7-Oxabicyclo[2.2.1]heptane (7) may be considered as *cis*-2,5-dimethyltetrahydrofuran with the methyl groups bound together in a bridge. Manipulation of Dreiding models indicates that considerable ring strain is introduced by the fusion, the effect being to reduce the COC angle toward the angle to be expected in trimethylene oxide. One manifestation of the high energy content of this molecule may be its high extractability into water from cyclohexane. Searles and Tamres[10] have observed the four-membered ring ether to exhibit greater basicity than tetrahydrofuran by several criteria and we were fully expecting a dramatic increase in basicity here. The low basicity of this compound relative to tetrahydrofuran (and therefore presumably to trimethylene oxide) is not compatible with what might be expected simply on the grounds of deformation of the COC angle but is consistent with the electron correlation interpretation we have presented above. One of the consequences of fusing the 2- and 5-methyl groups into a new ring is a twisting of the oxygen atom of what was the tetrahydrofuran ring so that the sp^3-orbitals occupied by the lone pair electrons are no longer eclipsed by the two hydrogens and two methyl groups that were present in *cis*-2,5-dimethyltetrahydrofuran. In 7-oxabicyclo[2.2.1]-heptane, in fact, the two lobes occupied by the lone pair are as neatly staggered with respect to nearby bonding pairs as they are in tetrahydro-

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[21] See for example: (a) R. J. Gillespie, *J. Am. Chem. Soc.*, **82**, 5978 (1960); (b) P. G. Dickens and J. W. Linnett, *Quart. Rev. Chem. Soc.*, **11**, 291 (1957); (c) G. H. Stewart and H. Eyring, *J. Chem. Ed.*, **35**, 550 (1958); (d) J. W. Linnett, *J. Am. Chem. Soc.*, **83**, 2643 (1961).

[22] G. Baddeley, J. Chadwick and H. T. Taylor, *J. Chem. Soc.*, 451 (1956).

[23] H. K. Hall, *J. Phys. Chem.*, **60**, 63 (1956), has made several independent measurements which are at variance with these findings.

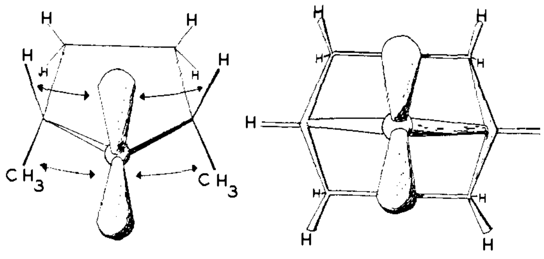

Fig. 2.

pyran (Fig. 2). From this point of view the free energy change associated with the protonation of 7-oxabicyclo[2.2.1]heptane should be similar to that for tetrahydropyran rather than tetrahydrofuran.

Dioxane *via-á-vis* Morpholine.—Dioxane is seen in Table I to be more basic than diethyl ether not only toward aqueous acid but also toward deuteriomethanol,[10] iodine[9] and in terms of its ability to dissolve hydrogen chloride.[14] However, when the basicities are measured by the Henry's law constants extrapolated to infinite dilution[15] or the influence on the proton resonance spectrum of water dissolved in the ether,[24] the order is reversed. In all cases studied so far dioxane is less basic than tetrahydropyran although the difference is often a modest one.

The relatively high basicity of dioxane in the oxygen base series contrasts sharply with the position of morpholine among the amines. Hall[25] has found morpholine to be over seven hundred times less basic than piperidine, the same order being observed also[26] for N-methylpiperidine and N-methylmorpholine. Using Hall's σ^*-values for cyclic systems based on his data for amines,[25] one might expect that the dioxonium ion should have a pK_a as low as -7 or -8 instead of -3.16 (the observed value after correction for the fact that it has two basic sites).[16] Hall has also shown[26] that monoethanolamine is a good deal more basic than morpholine and that a number of other cyclic amines with electronegative groups are less basic than their acyclic analogs, thus providing evidence for the incursion of a direct field effect. Our results for 1,2-dimethoxyethane when compared with dioxane show that in the case of the ethers there is virtually no change in basicity bestowed on the system by cyclization.

Although the other cyclic ethers described here give K_D' values which fall close to the linear relation of log K_D' *versus* parachor described in the paper previous to this one,[6] the two diethers fall very far below the line. This indicates that relative to the other ethers they are both abnormally soluble in water relative to cyclohexane.

If it is true that dioxane is indeed abnormally basic (and soluble in water), rather than morpholine being abnormally non-basic, a special cooperative influence of the oxygens in their interactions with water and hydronium ions is suggested. Some evidence for this may be found in the claims that dioxane forms stable compounds with aqueous phosphoric acid[27] and perchloric acid.[28]

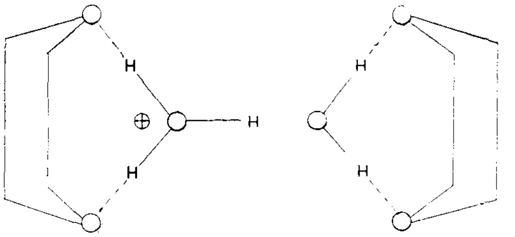

Fig. 3.

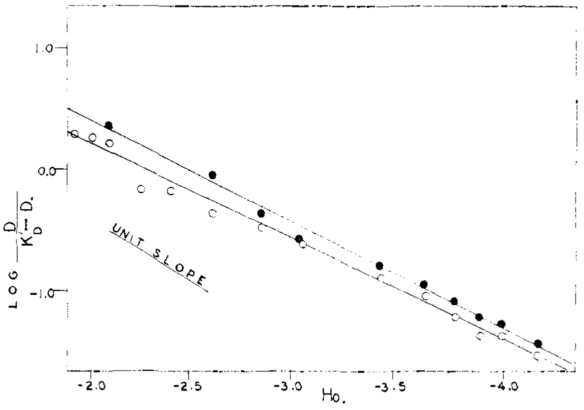

Fig. 4.

It may very well be that the high basicity and high water solubility of dioxane and 1,2-dimethoxyethane result from their ability to form unusually symmetrical hydrogen-bonded structures (Fig. 3). These representations are strongly reminiscent of those suggested by Grunwald, Baughman and Kohnstam[29] to account for the remarkable ability of dioxane to solvate ions. Supporting evidence for their reality can be found in the study of Errera, Gaspart and Sack[30] who observed splitting of the infrared O–H stretching band of water when dissolved in dioxane. Since the splitting vanished when HOD was used instead, these authors concluded that a symmetrical hydrogen bonding system was involved, presumably with both hydrogens bonded to the same dioxane molecule.

Experimental

The methods used for the purification of the ethers, the preparation of the sulfuric acid solutions and the purification of the cyclohexane used for solvent extraction were the same as described previously,[5,6] as also was the solvent extraction–g.l.c. procedure.

Materials.—Tetrahydrofuran, 2-methyltetrahydrofuran, dioxane and 1,2-dimethoxyethane were purchased from the Fisher Scientific Co. in the best grade available. Tetrahydropyran was bought from K. and K. Laboratories. A generous sample of 7-oxa[2.2.1]bicycloheptane was given to us by Dr. H. K. Hall, Jr., of the Pioneering Research Division of E. I. du Pont de Nemours Co. We appreciate his kindness.

Hexamethylene oxide was prepared from Fisher Co. hexane-1,6-diol by the procedure of Kirrmann and Ham-

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(24) M. G. Mavel, *J. chim. phys.*, **57**, 649 (1960). For a valuable review on basicities of oxygen compounds by this author, see *ibid.*, **58**, 545 (1961).

(25) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **79**, 5441 (1957).

(26) H. K. Hall, Jr., *ibid.*, **78**, 2570 (1956).

(27) B. Helferich and U. Baumann, *Chem. Ber.*, **85**, 461 (1952).

(28) C. Smeets, *Natuurw. Tijdschr.*, **19**, 12 (1937); *C. A.*, **31**, 1815 (1937).

(29) E. Grunwald, G. Baughman and G. Kohnstam, *J. Am. Chem. Soc.*, **82**, 5801 (1960).

(30) J. Errera, R. Gaspart and H. Sack, *J. Chem. Phys.*, **8**, 63 (1940).

TABLE II

EXTRACTION AND GAS CHROMATOGRAPHY DATA

Ether	pK_a	% H_2SO_4 at pK_a	$K_D'^a$	Slope of log plot^a	Concn. of stock soln., vol. %	Column^b packing	Column temp., °C.	Flow rate, ml./min.
Hexamethylene oxide	−2.02	33	68	0.88	1.5	T	106	60
Tetrahydrofuran	−2.08	35	2.65	.92	2	P	63	90
2,5-Dimethyltetrahydrofuran								
cis	−2.44	40	25.0	.80	4	P	50	120
trans	−2.65	43	29.5	.84	4	P	50	120
2-Methyltetrahydrofuran	−2.65	43	6.60	.86	2	P	68	70
Tetrahydropyran	−2.79	43	14.0	.76	2	T	82	80
7-Oxa[2.2.1]bicycloheptane	−2.80	44	6.27	.93	2	P	82	96
Dioxane	−3.16	48	0.21	.83	1	T	90	75

[a] See ref. 6 for the meaning of these symbols. Conditions for extraction and gas chromatography are the same as in previous papers: cyclohexane as solvent, Burrell K-2 Kromotog with 6-foot column and helium as carrier gas. [b] Burrell Corp. packings: P, polyethylene glycol on Celite; T, Tween on Celite.

TABLE III

SOLVENT EXTRACTION OF THF FROM CYCLOHEXANE AT 20°

% H_2SO_4	H_0	D	$\log \frac{D}{(K_D' - D)}$	pK_a
18.40	−1.00	2.480	1.140	−2.14
24.97	−1.34	2.334	0.548	−1.89
33.69	−1.95	1.950	.190	−2.14
35.24	−2.07	1.429	.131	−2.20
39.70	−2.39	1.034	− .563	−1.83
43.54	−2.74	0.798	− .731	−2.01
46.82	−3.06	.598	− .804	−2.26
48.84	−3.26	.486	− .832	−2.43

aide.[31] It was purified by distillation until homogeneous to gas chromatography. 2,5-Dimethyltetrahydrofuran was made by the cyclization of hexane-2,5-diol using the method of Reynolds and Kenyon.[32]

When this was subjected to gas chromatography under the conditions given in Table II, two cleanly separated peaks of equal size were obtained corresponding to the *cis* and *trans* isomers. This offered the opportunity of measuring the basicities of the two compounds without actually separating them. The results of this study are presented in Fig. 4 in the form of the customary plot[6] of $\log [D/(K_D' - D)]$ *versus* H_0. The material with the longer retention time was assigned the *cis* configuration in view of its lower K_D' value. According to our previous observations[6] this indicates that it also has a lower parachor and, if the empirical relationship of Gillespie, Macbeth and Mills[33] holds here, it may be taken to be the *cis* isomer.

It is clear from this example that if it is possible to find a g.l.c. column which permits resolution of a group of volatile bases it is practical to determine their basicities simultaneously by the extraction method without separating the individual bases beforehand.

In Table III are presented typical data for determination of the pK_a of THF oxonium ion.

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(31) A. Kirrmann and N. Hamaide, *Bull. soc. chim. France*, 789 (1957).

(32) D. D. Reynolds and W. O. Kenyon, *J. Am. Chem. Soc.*, **72**, 1593 (1950).

(33) D. T. C. Gillespie, A. K. Macbeth and J. A. Mills, *J. Chem. Soc.*, 280 (1940).

[CONTRIBUTION NO. 54 FROM THE EXPLORATORY RESEARCH LABORATORY, DOW CHEMICAL OF CANADA, LTD., SARNIA, ONTARIO, CAN.]

Aromatic Substitution. X.[1] The $AlCl_3 \cdot CH_3NO_2$-Catalyzed Benzylation of Benzene and *n*-Alkylbenzenes with Benzyl Chloride in Nitromethane Solution

BY GEORGE A. OLAH, STEPHEN J. KUHN AND SYLVIA H. FLOOD

RECEIVED OCTOBER 25, 1961

Competitive $AlCl_3 \cdot CH_3NO_2$-catalyzed benzylation of benzene and *n*-alkylbenzenes with benzyl chloride in homogeneous nitromethane solution has been investigated. Relative reactivities and isomer distributions were determined by gas–liquid chromatography, using when necessary a Golay type capillary column and hydrogen flame ionization detector. The observed relative rates, the reactions being first order in aromatic hydrocarbons, show good correlation with relative π-complex stabilities of alkylbenzenes, but not with σ-complex basicities. In the investigated low substrate selectivity reactions the amount of *meta* isomer formed was as low as 3.5 and not larger than 8.6%. Partial rate and selectivity factors are not applicable to the present systems (primary competition takes place between the π-electron systems of competing molecules as entities). The benzylation of benzene-d_6 shows a small secondary, direct kinetic isotope effect. The mechanism of the reaction is discussed in the light of the experimental results.

Introduction

The mechanism which for a long time was generally accepted for Friedel–Crafts type alkylation with alkyl halides involved ionization of the alkyl halide under the influence of the "acid" catalyst followed by electrophilic substitution of the aromatic nucleus by the carbonium ion.[2] A fundamental kinetic study by Brown and Grayson[3] of the reaction of benzyl halides with various aromatic compounds under the catalytic influence of aluminum chloride in nitrobenzene solution revealed that the reaction is third order—first order in aromatic component, first order in aluminum chloride and first order in the benzyl halide. Both benzyl chloride and *p*-chlorobenzyl chloride were found to react too rapidly for convenient rate measurement. Therefore 3,4-dichloro- and

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(1) Part IX, *J. Am. Chem. Soc.*, **83**, 4581 (1961).

(2) C. C. Price, *Chem. Revs.*, **29**, 37 (1941); "Organic Reactions," Vol. 3, John Wiley and Sons, Inc., New York, N. Y., pp. 1–82.

(3) H. C. Brown and M. Grayson, *J. Am. Chem. Soc.*, **75**, 6285 (1953).