manner.[18] Only **3** could be detected in the nmr spectrum of crude product, which was obtained in a near quantitative yield.

Recrystallization from cyclohexane-benzene gave an analytical sample, mp 93°.

Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 75.05; H, 5.05.

Analytical Procedure.—The nmr samples were made by dissolving *ca.* 70 mg of the ether in 1.0 ml of $CDCl_3$ and adding the shift reagent (Norell Chemical Co., stored over P_2O_5) in quantities up to 0.2 equiv. Dreiding models were used to estimate distances and angles. Angles were both measured directly and checked by appropriate geometric relationships.

Statistical Correlations.—A calculation of an agreement factor R was accomplished in a manner similar to the procedure employed by Willcott and Davis.[13] As mentioned in the Discussion, the lanthanide was moved in a plane bisecting the ethers **1**, **2**, and **3** at a distance of 3.0 Å from the coordination site. At each position of Ln, the variable term $\Delta H_i = \alpha(3 \cos^2 \theta_i - 1)/R_i^3$ was evaluated for all the ith protons to yield a set of calculated $(\Delta H/H)_{ci}$ values (α is a constant). A minimum value of R was then obtained by the best least-squares fit for

$$R = \left\{ \frac{\sum_i \left[\left(\frac{\Delta H}{H}\right)_{oi} - \left(\frac{\Delta H}{H}\right)_{ci} \right]^2}{\sum_i \left(\frac{\Delta H}{H}\right)_{oi}^2} \right\}^{1/2}$$

where $(\Delta H/H)_{oi}$ are observed shifts.

Registry No.—**1**, 573-57-9; **2**, 35185-96-7; **3**, 13137-34-3; $Eu(dpm)_3$, 15522-71-1; $Eu(fod)_3$, 17631-68-4; $Pr(fod)_3$, 17978-77-7.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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[18] L. F. Fieser and M. Fieser, "Organic Reagents," Vol. 1, Wiley, New York, N. Y., 1967, p 135.

Hydrogenolysis of Acetals and Ketals by Alkoxyalanes and Alkoxychloroalanes[1]

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The hydrogenolysis of acetals, ketals, and 1,3-dioxolanes was examined using alkoxy-substituted alanes. Alkoxychloroalanes are moderately reactive and show potential as stereoselective reducing reagents. Alkoxyalanes were less reactive and dialkoxyalanes too unreactive for hydrogenolysis.

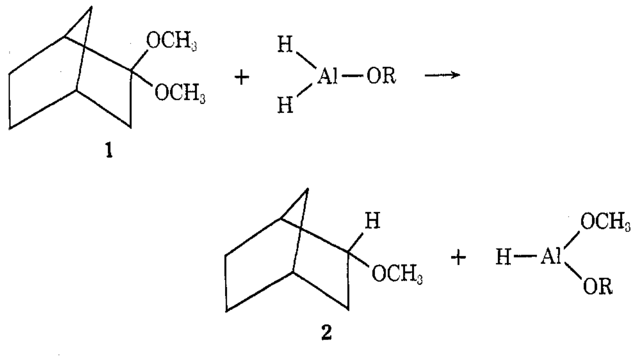
Cyclic and acyclic acetals and ketals can be hydrogenolyzed to the corresponding ethers by alane, chloroalane, and dichloroalane.[2] Having previously examined what structural features in the ketals affect the hydrogenolysis reaction,[3,4] we turned our attention to what structural modifications in the hydrogenolyzing reagent might affect the course of the reaction. Chloro groups are known to increase the reactivity of alanes.[5] Since oxygen and chlorine have similar electronegativities, we have investigated the use of alkoxyalanes, dialkoxyalanes, and alkoxychloroalanes for hydrogenolyzing acetals and ketals.

Isopropoxyalane and diisopropoxyalane have been prepared from the proper ratios of alane and triisopropoxyalane.[6] Ethoxyalane and diethoxyalane were prepared in a similar manner.[7] Many of the simpler alkoxyalanes and dialkoxyalanes have been prepared by the addition of 1 or 2 molar equiv of the corresponding alcohols to alane in THF.[8] The alkoxyalanes and dialkoxyalanes have been characterized by elemental analyses, molecular weight determinations, nmr and ir spectra,[6,8] and X-ray diffraction patterns.[7]

Early work showed dialkoxyalanes to be selective reagents which will reduce aldehydes, ketones, and acid chlorides, but not esters, nitriles, amides, nitrates, or aryl halides.[9] The use of alkoxyalanes has been extended to the reduction of epoxides.[10] The lone acetal reaction reported is the hydrogenolysis of 2-methyl-1,3-dioxolane by chloroethoxyalane.[11]

Results and Discussion

The hydrogenolysis of norcamphor dimethyl ketal (**1**) to 2-*endo*-norbornyl methyl ether (**2**) was examined



using various alkoxyalanes and solvents to find the best conditions for the hydrogenolysis of acetals and ketals. These exploratory results are listed in Table I. First it can be seen that the dialkoxyalanes are less reactive than the alkoxyalanes. Secondly, Table I shows that none of the alkoxyalanes are as reactive as the parent compound, alane. Thirdly, the results show that both ether and benzene are better solvents than is THF.

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[1] Taken from the Ph.D. Thesis of K. J. B., Villanova University, 1972.

[2] M. N. Rerick, "Reduction," R. L. Agustine, Ed., Marcel Dekker, Inc., New York, N. Y., 1968, pp 46–50.

[3] W. W. Zajac, Jr., and K. J. Byrne, *J. Org. Chem.*, **37**, 521 (1972).

[4] W. W. Zajac, Jr., and K. J. Byrne, *ibid.*, **35**, 3375 (1970).

[5] (a) U. E. Diner, H. A. Davis, and R. K. Brown, *Can. J. Chem.*, **45**, 207 (1967); (b) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, p 48.

[6] E. E. Flagg and D. L. Schmidt, *J. Inorg. Nucl. Chem.*, **31**, 2329 (1969).

[7] N. E. Matzek and W. H. Crawford, U. S. Patent 3,524,870 (1970); *Chem. Abstr.*, **73**, 98379k (1970).

[8] H. Noth and H. Suchy, *Z. Anorg. Allg. Chem.*, **358**, 44 (1968).

[9] M. W. Hunt, U. S. Patent 3,281,443 (1966); presented at Midwest Regional Meeting of the American Chemical Society, Lincoln, Nebr., Oct 1970.

[10] B. Cooke, E. C. Ashby, and J. Lott, *J. Org. Chem.*, **33**, 1132 (1968).

[11] H. A. Davis and R. K. Brown, *Can. J. Chem.*, **49**, 2166 (1971).

TABLE I
HYDROGENOLYSIS OF NORCAMPHOR DIMETHYL KETAL

Alane	Solvent[a]	% Hydrogenolysis
$\mathrm{H_2AlOMe}$	THF	<1[b]
$\mathrm{H_2AlOEt}$	THF	<1
$\mathrm{H_2AlO}$-*t*-Bu	THF	<1
$\mathrm{HAl(O}$-*t*-$\mathrm{Bu)_2}$	THF	<1
$\mathrm{H_3Al}$	Ether	100
$\mathrm{H_2AlOMe}$[c]	Ether	39
$\mathrm{H_2AlOEt}$	Ether	10
$\mathrm{H_2AlO}$-*i*-Pr	Ether	21
$\mathrm{H_2AlO}$-*t*-Bu	Ether	2.4
$\mathrm{H_2AlOCH_2CH_2OCH_3}$	Ether	9
$\mathrm{HAl(OEt)_2}$	Ether	1
$\mathrm{H_2AlOMe}$	Benzene	8.5
$\mathrm{H_2AlO}$-*i*-Pr	Benzene	58
$\mathrm{HAl(O}$-*i*-$\mathrm{Pr)_2}$	Benzene	<1

[a] Room temperature for 22 hr. [b] 100 hr at reflux temperatures gave 76% hydrogenolysis. [c] Methoxyalane gave 46% hydrogenolysis of norcamphor diethyl ketal to 2-*endo*-norbornyl ethyl ether at room temperature for 22 hr in ether. Dimethoxyalane gave only 1% hydrogenolysis after 48 hr in refluxing ether.

The alkoxyalanes and dialkoxyalanes have been studied in THF and benzene and found to exist as dimers, trimers, and insoluble polymers depending on the alkoxy groups.[6,8] They are associated into these aggregates by bridge bonding of the alkoxy oxygens. Chloroalane and dichloroalane exist in diethyl ether as monomeric etherates.[12] In the first step of hydrogenolysis an alane must complex with an acetal. The complex opens to give an oxocarbonium ion intermediate which reacts with a hydride to give an ether product. An alane must be available to form the initial acetal complex. The alkoxyalanes satisfy their Lewis acid nature by bridge bonding into aggregates even in a strong Lewis base such as THF. Clearly the equilibrium between such a stable aggregate and an acetal complex will be less favorable than the equilibrium between an etherate complex and acetal complex. Therefore, the low reactivity of the alkoxyalanes is explainable by the strength of the aggregates and corresponding small shift in the equilibrium to acetal–alane complexes. Because the strength of the different aggregates are unknown at this point, the hydrogenolyzing strengths of different alkoxyalanes are not easily predictable. Also the question of whether except for bridging an oxygen atom on alane has the same properties as a chlorine atom cannot be answered. Ashby found the alkoxyalanes to be less reactive than alane or chloroalane for the reduction of β-diisobutylene oxide and styrene oxide in THF.[10] In these reactions the dialkoxyalanes are even less effective.

Methoxyalane was the most reactive alkoxyalane for the hydrogenolysis of norcamphor dimethyl ketal in ether and it was used to study the reactivity of various acetals and ketals. The results of this study appear in Table II. The ortho ester is the most reactive. It is completely hydrogenolyzed in the presence of its product, benzaldehyde dimethyl acetal, which in itself is 61% hydrogenolyzed to benzyl methyl ether (there was an 80% excess of methoxyalane in all reactions). The reactivity of the acetals is what would be predicted for methoxyalane if it is analogous to chloroalane. The acetal or ketal that yields the more stabilized oxocarbonium ion intermediate is more reactive.[3,13] Thus, benzaldehyde dimethyl acetal is more reactive than aliphatic ketals, which in turn are more reactive than an aliphatic acetal. The open norcamphor dimethyl ketal is more reactive than the cyclic norcamphor ethylene ketal. Cyclododecanone dimethyl ketal gave 25% elimination of methanol to give a vinyl ether. Strained ring systems are prone to such elimination because it reduces the crowding of ring substituents and therefore strain. Cycloheptanone dimethyl ketal is a compound with considerable eclipsing strain.[4] This ketal was allowed to react for 22 hr at room temperature with methoxyalane in THF as well as in ether. In THF this very reactive ketal hydrogenolyzed 30% to cycloheptyl methyl ether. The elimination product, 1-cycloheptenyl methyl ether, amounted to 6%, while 64% of the ketal survived. In the more favorable solvent, diethyl ether, no ketal survived. There was 4.5% hydrogenolysis and 95.5% elimination to the vinyl ether. Since the Lewis acidity of the alane is involved in both the hydrogenolysis and elimination, methoxyalane appears to be a more effective Lewis acid in ether. The methoxyalane seems to be a good hydride donor in THF, but the predominance of the elimination product in ether suggests that the monomeric methoxyalane has lost much of its hydride donating ability in ether or that some other aluminum species is catalyzing the elimination in ether. Ashby has noted the strong hydride donor properties of alkoxyalanes in THF.[10]

TABLE II
HYDROGENOLYSIS OF ACETALS AND KETALS
BY METHOXYALANE

Acetal	Time,[a] hr	% Hydrogenolysis
Trimethylorthobenzoate	48	100[b]
Benzaldehyde dimethyl acetal	48	100
Norcamphor dimethyl ketal	48	96
Cyclododecanone dimethyl ketal	48	72[c]
Norcamphor ethylene ketal	48	55
Norcamphor ethylene ketal	168	73
Heptanal dimethyl acetal	48	24
Heptanal dimethyl acetal	168	53

[a] Refluxing ether. [b] The product was 61% benzyl methyl ether and 39% benzaldehyde dimethyl acetal. [c] The unhydrogenolyzed part was 3% ketal, 13% *trans*-1-cyclododecenyl methyl ether, and 12% *cis*-1-cyclododecenyl methyl ether.

2,2,4,4-Tetrasubstituted 1,3-dioxolanes such as **3**, **4**, and **5** give predominantly tertiary alcohol when they are hydrogenolyzed and not primary alcohol. For 2,2,4,4-tetramethyl-1,3-dioxolane (**3**), chloroalane complexes mainly with the more crowded oxygen (**6**) and opens to give the less inductively stabilized oxocarbonium ion intermediate (**7**).[14] This unusual route is believed to be due to the steric strain in **9** (resulting from the alternate complex **8**) which is not present in the intermediate **7**.

The hydrogenolysis of **3** by chloroalane is reported to give 6% primary alcohol,[14] and **4** to give exclusively tertiary alcohol.[15] When **3** was treated for 1 week

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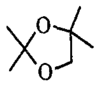
[12] (a) E. Wiberg, K. Modritzer, and R. Uson Lacel, *Rev. Acad. Cienc. Exactas, Fis-Quim. Natur. Zaragoza*, **9**, 91 (1954); (b) E. C. Ashby and J. Prather, *J. Amer. Chem. Soc.*, **88**, 729 (1966).

[13] B. E. Leggetter and R. K. Brown, *Can. J. Chem.*, **42**, 990 (1964).

[14] B. E. Leggether and R. K. Brown, *ibid.*, **42**, 1005 (1964).

[15] E. L. Eliel, V. G. Badding, and M. N. Rerick, *J. Amer. Chem. Soc.*, **84**, 2371 (1962).



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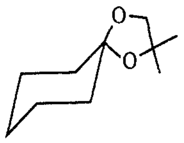

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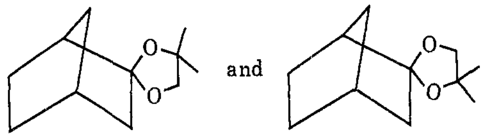

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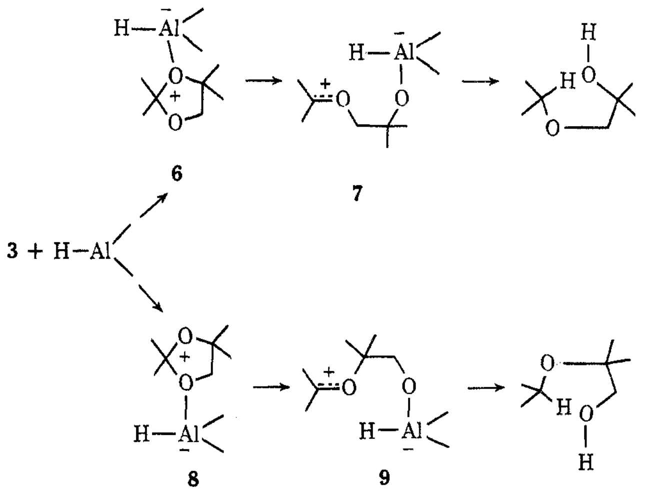

with methoxyalane in refluxing ether, there was 64% hydrogenolysis with 10% of the product being primary alcohol. Under the same conditions **4** was 23% hydrogenolyzed with 12% of the product being primary alcohol. This could indicate that methoxyalane has greater steric requirements than chloroalane or dichloroalane and complexes like **6** are less favorable. This is unlikely because chloromethoxyalane gives only 3.5% primary alcohol with **3** (Table III).

TABLE III

HYDROGENOLYSIS OF 2,2,4,4-TETRAMETHYL-1,3-DIOXOLANE BY SOME ALKOXYCHLOROALANES

Alane[a]	% Hydrogenolysis	% Primary alcohol
HAlClOMe	80	3.5
HAlClOEt	70	4.7
HAlClO-*i*-Pr	30	9.8
HAlClO-*t*-Bu[b]	11	24.4
$HAlClO(CH_2)_2OCH_3$[c]	<1	

[a] Refluxing ether for 2 hr. [b] When refluxed for 1 week norcamphor isobutylene ketal gave 10% hydrogenolysis with methoxyalane with 22% being exo primary alcohol and 78% endo tertiary alcohol. Chloroisobutoxyalane gave 59% hydrogenolysis with 42 and 58% of the two alcohols, respectively. Chloroalane is reported to give 32 and 68%, respectively: P. C. Loewen, W. W. Zajac, Jr., and R. K. Brown, *Can. J. Chem.*, **47**, 4059 (1969). [c] 2-methoxyethoxyalane gave 4% hydrogenolysis under the same conditions with 10% being primary.

Since dialkoxyalanes are relatively quite unreactive as hydrogenolyzing agents (Table I), several alkoxychloroalanes were examined to detemine if they would exhibit more selectivity. The results for the hydrogenolysis of 2,2,4,4-tetramethyl-1,3-dioxolane are listed in Table III. As the alkoxy group changes from Me to Et to *i*-Pr to *t*-Bu, the extent of hydrogenolysis decreases and the percentage of primary alcohols in the product increases. The increase of primary alcohol suggests that complex **6** is becoming more hindered as the alkoxy group becomes larger. It is not known whether alkoxychloroalanes are monomeric in ether or associated. The reactivity of a particular alkoxychloroalane would depend on the reactivity of the monomer and the association energy of larger aggregates if any. Since the reactivity falls off with larger alkoxy groups in a way which would be expected for the monomeric alanes, it appears that the aggregates, if they exist, dissociate to monomers about equally readily. The steady change in reactivity for alkoxychloroalanes and steady change in primary alcohol product rule out any possibility that the alkoxychloroalanes disproportionate and react through a common chloroalane or dichloroalane. No measurable hydrogenolysis was obtained with 2-methoxyethoxychloroalane (Table III). When this alane was prepared it formed a tacky precipitate, as has been reported.[11] In contrast 2-methoxyethoxyalane had about the same reactivity as ethoxyalane (Table I).

The alkoxychloroalanes are reactive hydrogenolysis reagents suitable for the hydrogenolysis of acetals and ketals. By using more substituted alkoxy groups in the alkoxychloroalane it has been possible to moderately alter the products of the hydrogenolysis of **3**. This family of reagents offers promise in the reduction of acetals, ketals, and other functional groups in which the reaction is subject to steric factors. Alkoxyalanes and dialkoxyalanes do not appear to have the general usefulness of chloroalane and dichloroalane, although the former will satisfactorily hydrogenolyze reactive acetals and ketals.

Experimental Section

Hydrogenolyses with Alkoxyalanes and Dialkoxyalanes.—Clear, standardized (~1.2 *M*) solutions of $LiAlH_4$ in THF and Et_2O were prepared as described by Brown and Weissman.[16] When standardizing the Et_2O solution the described ethylene glycol was replaced by 30 ml of bis(2-methoxyethyl) ether and 5 ml of 1-butanol stirring at 0°. A quantity of a standardized solution (~30 ml) containing 36 mmol was syringed into a 100-ml flask having a magnetic stirring bar, septum fitted neck, N_2 atmosphere, and adequate vent for N_2 and H_2.[17] THF or Et_2O were added to bring the volume to 60 ml. AlH_3 was prepared by syringing 0.96 ml (18 mmol) of 100% H_2SO_4 slowly to the flask in an ice bath. The Li_2SO_4 was not filtered out. After 0.5 hr without the ice bath it was returned and 36 mmol of an alcohol was syringed into the flask slowly to yield an alkoxyalane. This corresponds to 1.50 ml of MeOH, 2.20 ml of EtOH, 2.85 ml of *i*-PrOH, 3.50 ml of *t*-BuOH, or 2.95 ml of methoxyethyl alcohol. For dialkoxyalane 72 mmol of alcohol was used. For reactions in PhH, 60 ml of PhH was added in 10-ml portions to an alkoxyalane in Et_2O. The Et_2O was distilled out; when 60 ml of distillate was removed the thermometer temperature was 72°. The acetal or ketal (0.20 mmol) was syringed into the reagent when it was at the desired temperature. At work-up the reaction was poured into a separatory funnel containing 150 ml of ice water, 75 ml of Et_2O, and a small amount of K_2CO_3. The aqueous layer was extracted a second time with 75 ml of Et_2O. When dioxolanes were hydrogenolyzed, concentrated HCl was now added to the aqueous layer until the aluminum salts dissolved and 100 ml of Et_2O was used to extract the aqueous layer again, which was back extracted with 10 ml of 5% NaOH. The combined Et_2O extracts were washed with 50 ml of saturated NaCl and dried over K_2CO_3. After evaporation of solvent the products were identified

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[16] H. C. Brown and P. M. Weissman, *J. Amer. Chem. Soc.*, **87**, 5614 (1965).

[17] H. C. Brown and N. M. Yoon, *ibid.*, **88**, 1464 (1966).

by glpc comparison with known compounds or by collecting the glpc peaks for spectra. The percentage yields reported correspond to the peak area.

Hydrogenolyses with Alkoxychloroalanes.—Into the flask described above was weighed 2.40 g (18 mmol) of $AlCl_3$. In an ice bath 45 ml of Et_2O was syringed into the flask to dissolve the $AlCl_3$; 18 mmol of the standardized $LiAlH_4$ solution ($\sim$15 ml) was added by syringe. After 15 min without the ice bath it was returned, the alcohol was added, and the hydrogenolysis was run as above. For work-up the reaction mixture was poured into a separatory funnel containing 4 g of NaOH, 50 ml of H_2O, 50 g of ice, and 75 ml of Et_2O. The rest of the work-up was as above.

Materials.—THF and Et_2O were dried by distillation from $LiAlH_4$. Alcohols were distilled from CaH_2. The preparations of norcamphor dimethyl ketal, cycloheptanone dimethyl ketal, and cyclodecanone dimethyl ketal have been described.[4] The published preparation for 2,2,4,4-tetramethyl-1,3-dioxolane also yielded cyclohexanone isobutylene ketal and norcamphor isobutylene ketal.[18] The preparations of norcamphor diethyl ketal,[3] norcamphor ethylene ketal,[18] and trimethyl orthobenzoate[19] are reported. Benzaldehyde dimethyl acetal and heptanal dimethyl acetal were prepared from the aldehydes and trimethyl orthoformate.

Registry No.—**1**, 10395-51-4; **3**, 13372-34-4; methoxyalane, 36803-31-3.

(18) E. J. Salmi, *Ber.*, **71**, 1803 (1938).

(19) S. M. McElvain and J. T. Venerable, *J. Amer. Chem. Soc.*, **72**, 1661 (1950).

The Vapor Phase Pyrogenesis of Phenol

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Phthalic acid and 3- and 4-methylphthalic acids (precursors of benzyne, methylbenzyne, water) were pyrolyzed at 700° and their interaction products were determined. From phthalic acid, the major products, in addition to benzyne interaction products, were benzoic acid, phenol, and phenyl benzoate. It is proposed that decarboxylation of phthalic acid competes with benzyne formation *via* the anhydride and that phenol and phenyl benzoate arise through a competitive addition of water and benzoic acid, respectively, to the benzyne intermediate. The vapor phase addition of water to methylbenzynes produces the expected isomeric cresols.

The high-temperature pyrolysis (*ca.* 800°) of a number of natural products such as tobacco,[1] lignin,[2] and carbohydrates[3] has been reported to produce significant amounts of phenol and substituted phenols. Because of the reported activity of phenols as tumor-promoting agents,[4] the origin of these substances in the pyrolytic process is of considerable interest. It was recently found that the pyrosynthesis of phenols occurs when both aromatic and nonaromatic substances, such as amino acids[5a] and maleic hydrazide,[5b] are pyrolyzed at high temperatures. The presence of hydrocarbons in the pyrolysate, which have been shown to arise from benzyne, suggested that benzyne might be a precursor to the phenols observed in the high-temperature pyrolyses. While the addition of water to benzyne in the liquid phase has been adequately demonstrated,[6] no evidence was available to indicate that the addition would occur in the vapor phase at high temperatures (700°) or in what way. Because of the recent reports that the addition of carbon disulfide to benzyne gives different products in the vapor phase[7] as compared to the liquid phase,[8] the possible vapor phase addition of water to benzyne was investigated.

Results and Discussion

The ease with which phthalic acid undergoes dehydration to phthalic anhydride and water and the fact that the thermal decomposition of phthalic anhydride at 700° produces benzyne[9] suggests that the pyrolysis of phthalic acid and methyl-substituted phthalic acids at 700° would provide convenient systems for observing the interaction of benzyne with water in the vapor phase.

When phthalic acid was pyrolyzed at 700°, phenol, phenyl benzoate, and benzoic acid were produced in addition to the usual benzyne products of biphenyl and naphthalene. Substituted phenols were likewise obtained from the thermolysis of 3- and 4-methylphthalic acids at 700°. The yields of these products as well as the relative concentrations of other pyrolysate constituents are summarized in Tables I and II.

TABLE I

YIELDS[a] OF SELECTED COMPONENTS OBTAINED FROM THE PYROLYSIS OF PHTHALIC ACID, BENZOIC ACID, AND METHYL-SUBSTITUTED DERIVATIVES AT 700°

Component	Phthalic acid	Benzoic acid	Toluic acids o-	Toluic acids m-	Toluic acids p-	Methylphthalic acids 3-	Methylphthalic acids 4-
Naphthalene	1.2						
Biphenyl	1.8						
Phenol	3.9	0.4				0.09	0.14
o-Cresol			0.01	*b*	*b*	0.10	*b*
m-Cresol			*b*	0.02	*b*	0.11	
p-Cresol			*b*	*b*	0.01	*b*	1.25[c]
Phenyl benzoate	2.2						

[a] Yields are reported as moles of compound per mole of substance pyrolyzed × 100 and were determined by glpc using internal standards. [b] Not found. [c] Mixture of *m*- and *p*-cresol incompletely resolved by glpc. Ratio of para to meta isomer as determined by infrared spectroscopy was 0.83:1.

It is proposed that the major reaction products arise through a competitive decarboxylation and de-

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(1) R. L. Stedman, *Chem. Rev.*, **68**, 153 (1968).

(2) W. S. Schlotzhauer, I. Schmeltz, and L. C. Hickey, *Tobacco Sci.*, **11**, 31 (1967).

(3) E. B. Higman, I. Schmeltz, and W. S. Schlotzhauer, *J. Agr. Food Chem.*, **18**, 639 (1970).

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