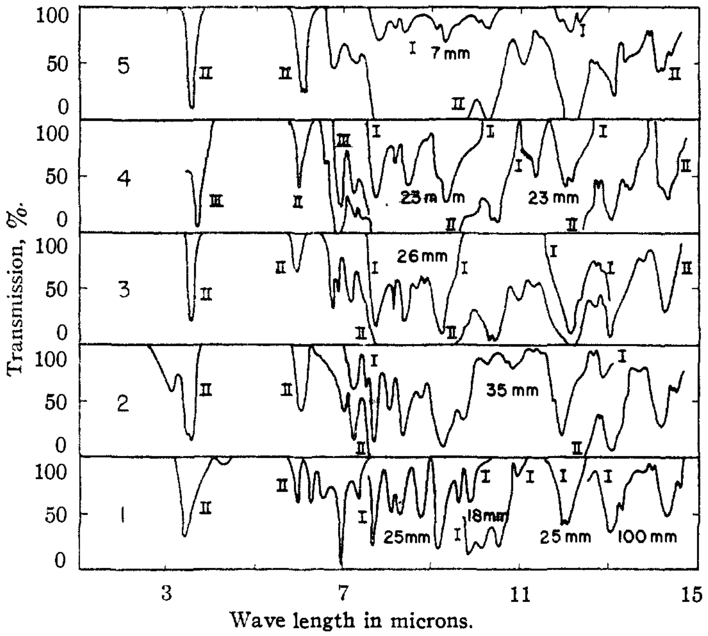

Fig. 2.—The infrared absorption spectrograms at room temperature: I in a 10–cm. gas cell at ind., press., II in a 0.025 mm. liquid cell, and III in a 0.1 mm. liquid cell of (1) CH_3-O-CF_2CHCl_2, (2) C_2H_5-O-CF_2CHCl_2, (3) C_3H_7-O-CF_2CHCl_2, (4) *n*-C_4H_9-O-CF_2CHCl_2, and (5) *n*-C_5H_{11}-O-CF_2CHCl_2.

starting olefin was obtained by dehydrochlorination of CF_2Cl–$CHCl_2$ using a previously described pyrolysis method,[6a,b,c] which consisted of passing CF_2Cl–$CHCl_2$ through a Pyrex tube (65 cm. × 9 mm. i.d.) heated to 650° to give yields of 60–75% of CF_2=CCl_2 per pass at a contact time of 8–10 seconds.

Some of the physical properties of the ethers are listed in Table I.

TABLE I

PHYSICAL PROPERTIES OF 1,1-DIFLUORO-2,2-DICHLOROETHYLALKYL ETHERS. R—O—CF_2—$CHCl_2$.

R	F.p.	B.p., °C.	B.p., Mm.	d^{20}_4	$n^{25}d$	$M_r a$	$M_r b$	$A_r F c$
-CH_3[d]		104	760	1.4226	1.3864	27.26	27.29	1.01
-C_2H_5[e]	Glass	120	760	1.3461	1.3895	31.51	31.91	0.83
-C_3H_7	Glass	136.5	760	1.2636	1.3968	36.79	36.53	1.16
-C_4H_9	Glass	153	760	1.2184	1.4029	41.79	41.15	1.19
-C_5H_{11}	Glass	172.5	760	1.1817	1.4157	49.51	48.74	1.41

R	Chlorine, % Calcd.	Chlorine, % Found	Molecular weight Calcd.	Molar susceptibility × 10^6 Calcd.	Molar susceptibility × 10^6 Found
-CH_3	42.99	42.76	164.99	− 97.53	− 80.68
-C_2H_5	39.61	39.61	179.02	−109.39	− 96.13
-C_3H_7	36.73	36.48	193.05	−121.25	−107.19
-C_4H_9	34.24	34.28	207.08	−133.11	−119.48
-C_5H_{11}	32.07	31.88	221.11	−144.97	−129.84

[a] M_r denotes the molecular refraction calculated by the Lorentz–Lorenz formula. [b] M_r denotes the molecular refraction calculated by adding the customary increments for C, H, O, F and double bond (F = 1.03). [c] A_rF is the atomic refraction of fluorine, obtained from $M_r a$ by subtracting the customary increments for C, H, O and the double bond. [d] W. T. Miller, E. W. Fager and P. H. Griswold, THIS JOURNAL, 70, 431 (1948). [e] T. B. Gowland, British Patent 523,449; *C.A.*, 35, 6265 (1941).

The ultraviolet absorption spectra of the ethers were measured with a Beckman quartz spectrophotometer model DU. The measurements were made on the pure liquids with an empty reference cell. The quartz cells were 1 cm. long. The extinction coefficient, E, defined by $\log I/I_0 = -El$ was measured; l is the length of the cell in cm. (unity in the present case). The results are given in Fig. 1.

The infrared absorption spectra were measured using an automatic recording Perkin–Elmer infrared spectrometer, model 12B with beam chopper attached. The samples were run in a 0.1 mm. liquid cell, a 0.025 mm. liquid cell or in a 10 cm. gas cell. The results are given in Fig. 2 where per cent. transmission is plotted against wave length in microns. Some qualitative assignments of the peaks are possible using the data of Barnes, *et al.*[7] The strong absorption appearing at 3.37–3.68 microns is due to C–H stretching in alkyl groups. A C–H bending absorption appears at 6.78–6.93. The absorption due to C–O stretching in a saturated ether is strong in the region 9.22–9.32 and is characteristic. The molar diamagnetic susceptibilities measured by the Quincke tube method[8] show a fairly constant deviation from the additive values obtained using Pascal's constants. This deviation is probably due to interaction forces between non-bonded atoms directed along the edges of a tetrahedron.[8,9]

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(6) (a) P. Torkington and H. W. Thompson, *Trans. Faraday Soc.*, **41**, 236 (1945); (b) F. B. Downing, A. F. Benning and R. C. McHarness, U. S. Patent 2,387,247; (c) A. F. Benning, F. B. Downing and J. D. Park, U. S. Patent 2,406,794.

(7) R. B. Barnes, R. C. Gore, R. W. Stafford and V. Z. Williams, *Anal. Chem.*, **20**, 402 (1948).

(8) J. R. Lacher, R. E. Scruby and J. D. Park, THIS JOURNAL, **71**, 1797 (1949).

(9) J. R. Lacher, *ibid.*, **69**, 2067 (1947).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF COLORADO
BOULDER, COLORADO

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Aromatization of Cyclic Compounds by Solid Potassium Perchlorate

BY SAUL PATAI AND LEON RAJBENBACH

In the course of a study of heterogeneous oxidation processes by solid inorganic oxidants[1] we have investigated the reaction of solid potassium perchlorate with aromatic hydrocarbons such as toluene, naphthalene and phenanthrene. Such compounds are generally oxidized without difficulty to the corresponding acids or quinones by various oxidants. Although potassium perchlorate is a powerful oxidizing agent, heating at 370–440° left the mixtures practically unchanged apart from the production of small amounts of potassium chloride and some carbonaceous material. At higher temperatures, approaching the decomposition temperature of potassium perchlorate (510°[2]), very rapid reaction takes place resulting in the explosion of the glass ampoules used.

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(1) Patai and Hoffmann, THIS JOURNAL, **72**, 5098 (1950).

(2) Marvin and Woolaver, *Ind. Eng. Chem.*, *Anal. Ed.*, **17**, 474 (1945).

TABLE I

DEHYDROGENATION BY SOLID POTASSIUM PERCHLORATE

Organic compound, grams	$KClO_4$, g.	Reaction time, hr.	Reaction temp., °C.	Product (identification)	Yield,[a] % A	B
4.8 Tetralin	10	18	370	Naphthalene (picrate)	94	87
1.75 Decalin	4.4	18	380	Naphthalene (picrate)	58	92
4.1 Cyclohexene	5	24	350	Benzene (*m*-dinitrobenzene)	5[b]	13[b]
1.9 Cyclohexanol	7.5	14	380	Phenol (tribromophenol)	4.8	22
1.9 Cyclohexanone	7.5	9	375	Phenol (tribromophenol)	2.5	2.5
1.8 3-Methylcyclohexanone	7.5	13	375	*m*-Cresol (tribromocresol)	17	14

[a] Yield A calculated on basis of the organic starting material, yield B calculated on basis of the amount of potassium perchlorate which decomposed (determined as chloride). [b] Dinitration of benzene in the presence of cyclohexene gave poor yields. The actual yield of benzene was probably much higher than the stated value.

In an attempt to obtain phthalic acid from tetralin instead of naphthalene, the reaction surprisingly produced an excellent yield of naphthalene only.

The same reaction, *i. e.*, dehydrogenation to the corresponding aromatic compound, was observed on allowing potassium perchlorate to react at 350–380° with decalin, cyclohexene, cyclohexanol, cyclohexanone and 3-methylcyclohexanone. All reactions were carried out in heavy-walled Pyrex tubes, using an excess of potassium perchlorate (200 mesh). The closed tubes were inserted in iron tubes and heated in an electric furnace behind a steel protecting plate, as heavy explosions may occur due to accidental overheating or to faulty ampoules. The results of preliminary experiments are summarized in Table I. No systematic effort has been made to improve the yields.

The reaction of alicyclic compounds with solid potassium perchlorate appears to be a new route to the corresponding aromatic compounds. The mechanism of the reaction, as well as its possible synthetic applications are now being investigated.

DEPARTMENT OF ORGANIC CHEMISTRY
HEBREW UNIVERSITY
JERUSALEM, ISRAEL

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Studies on Lignin and Related Products. IV.[1] Separation of Syringaldehyde and Vanillin by Chromatography[2]

BY IRWIN A. PEARL AND EDGAR E. DICKEY

For many years the quantitative separation of syringaldehyde and vanillin from the bisulfite-soluble fractions of angiosperm lignin reaction mixtures has offered a problem to the lignin chemist. Hibbert and co-workers[3] have proposed a number of methods based upon differential solubilities of their potassium and ammonium salts in ethanolic solution and upon fractional sublimation in high vacuum. Bland[4] has reported recently the qualitative separation of syringaldehyde and vanillin by paper partition chromatography but this method is limited to very small quantities and its quantitative adaptation presents numerous difficulties. The present paper reports a relatively simple chromatographic procedure for the quantitative separation of these two aldehydes. The procedure is a modification of a general chromatographic method originally employed by McNeely, Binkley and Wolfrom[5] for the separation of sugar acetates. An acid washed Magnesol[6] absorbent and a petroleum ether–ethanol developer successfully separated these two aldehydes. The colorless zones were located by five streak reagents which were applied with capillary-tipped pipets in a manner similar to the brush technique. With these pipets it was possible to apply a narrow, uniform streak to the extruded columns.

All melting points are uncorrected.

Acid-washed Magnesol.[7]—A mixture of Magnesol and Celite No. 535[8] (5:1 by weight) was prepared and suspended with mechanical stirring in sufficient dilute hydrochloric acid (1:3) to form a free-flowing slurry. The slurry was filtered on a Büchner funnel and washed with distilled water until free of chloride ions (by the silver nitrate test). The water was displaced with acetone, and the adsorbent was air dried at room temperature overnight and then at 110° for an additional 18 hours.

Separation of Vanillin and Syringaldehyde.—A solution of 23.4 mg. of syringaldehyde and 25.2 mg. of vanillin in 5 ml. of benzene was adsorbed on a column (18 mm. in diameter and 140 mm. long) of acid-washed Magnesol, and the

TABLE I

STREAK REAGENTS APPLIED TO CHROMATOGRAMS OF SYRINGALDEHYDE AND VANILLIN

Reagent	Behavior with syringaldehyde	vanillin
2,4-Dinitrophenylhydrazine (satd. solution in 2 *N* HCl)	Deep orange	Deep orange
Potassium permanganate (1% $KMnO_4$ in 10% aqueous NaOH)	Fast reduction	Slow reduction
Phloroglucinol (satd. solution in concd. HCl)	Orange-red	Orange-red
Ferric chloride (5% $FeCl_3$ in water)	Very light gray	No reaction
Mäule test (satd. chlorine water followed in 2 min. by 5% aqueous sodium sulfite)	Cerise	No reaction

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(1) For Part III of this series, see THIS JOURNAL, **72**, 2309 (1950).

(2) This paper represents a portion of the results obtained in the research program sponsored by the Sulphite Pulp Manufacturers' Research League and conducted for the League by The Institute of Paper Chemistry. Acknowledgment is made by the Institute for permission on the part of the League to publish these results.

(3) (a) M. J. Hunter and H. Hibbert, THIS JOURNAL, **61**, 2190 (1939). (b) J. J. Pyle, L. Brickman and H. Hibbert, *ibid.*, **61**, 2198 (1939). (c) R. H. J. Creighton, J. L. McCarthy and H. Hibbert, *ibid.*, **63**, 3049 (1941).

(4) D. E. Bland, *Nature*, **164**, 1093 (1949).

(5) W. H. McNeely, W. W. Binkley and M. L. Wolfrom, THIS JOURNAL, **67**, 525 (1945).

(6) A synthetic hydrated magnesium acid silicate manufactured by Westvaco Chlorine Products Company, South Charleston, West Virginia.

(7) This procedure was developed by one of the authors (E. E. D.) in the laboratory of Dr. M. L. Wolfrom at The Ohio State University.

(8) A siliceous filter-aid manufactured by Johns-Manville Company, New York, N. Y.