talline dibromo product which must be 1-hydroxy-3-methoxy-4,6-dibromobenzene (I), since its methylation yields 4,6-dibromoresorcinol dimethyl ether.[1] The nitration of I yields a nitrodibromoresorcinol monomethyl ether, which according to the method of preparation should be 1-hydroxy-2-nitro-3-methoxy-4,6-dibromobenzene (II). The m.p. of this substance is, however, very close to the melting point of the isomeric 1-hydroxy-3-methoxy-2,4-dibromo-6-nitrobenzene (III) reported by Kohn and Loeff.[2,3] The nitration of purest 2,4,6-tribromoresorcinol monomethyl ether (IV) produces an identical substance. Therefore in the nitration of I a migration of the bromine atom from
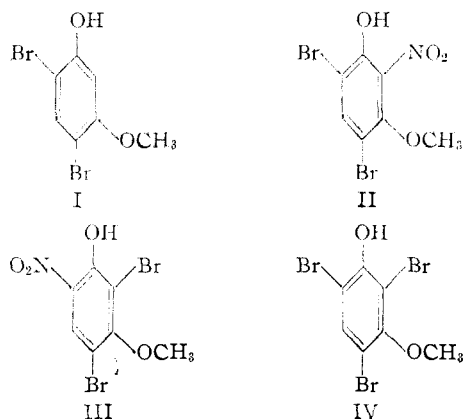
position 6 into position 2 takes place. A similar rearrangement was observed by Hodgson and Dyson[4] who found that the nitration of the 3-monobenzoate of 4,6-dibromoresorcinol leads to the 2,4-dibromo-6-nitroresorcinolmonobenzoate.

Reduction of tribromoresorcinol monomethyl ether (IV) with zinc dust and acetic acid removes the bromine atom between the OH– and the OCH_3–group forming I. Thus the reduction of IV proceeds in the same way as the reduction of 2,4,6-tribromoresorcinol, whereby 4,6-dibromoresorcinol[5] is formed.

Experimental

4,6-Dibromoresorcinol Monomethyl Ether (I).—Resorcinol monomethyl ether (19.5 g.) is dissolved in 60 cc. of chloroform, the mixture cooled in an ice-bath and a cooled solution of 16 cc. of bromine in 60 cc. of chloroform is slowly added through a dropping funnel with continuous stirring. After 6 hours the chloroform is evaporated on a steam-bath. The residue is triturated with low boiling petroleum ether and the solid is collected (31 g.). After removal of the petroleum ether by evaporation an oily residue is obtained (about 10 g.). This oil yields by bromination in glacial acetic acid tribromoresorcinol monomethyl ether (IV) (10 g., m.p. 105° after recrystallization).

By recrystallization of 10 g. of the crude dibromoether from petroleum ether 6 g. of the pure substance is obtained; colorless prisms, m.p. 73–75°.

Anal. Calcd. for $C_7H_6O_2Br_2$: Br, 56.73. Found: Br, 56.65.

The substance is very difficultly soluble in boiling water, more easily when diluted with alcohol or methanol. Its methylation yields 4,6-dibromoresorcinol dimethyl ether,[1] m.p. 141–143°.

1-Hydroxy-3-methoxy-2,4-dibromo-6-nitrobenzene (III).—One and nine-tenths grams of I is dissolved in 15 cc. of

glacial acetic acid and to this cooled solution a cooled mixture of 1.5 cc. of nitric acid in 10 cc. of glacial acetic acid is added. The liquid is kept in an ice-bath until the color turns light brown-yellow and is afterwards poured on 500 g. of ice. The solution is stirred until the oily precipitation solidifies. The crude product is collected, converted with potassium hydroxide into its red potassium salt, which is collected (1.4 g.) and then decomposed by diluted sulfuric acid. The yellow nitro product is recrystallized from alcohol; prisms, m.p. 123–126°.

Anal. Calcd. for $C_7H_5O_4NBr_2$: N, 4.29. Found: N, 4.03.

The m.p. of a sample prepared according to Kohn and Loeff[2] was 125–127°, its mixed m.p. with III prepared from I gives no depression.

Debromination of the tribromoresorcinol monomethyl ether (IV) is accomplished by dissolving 5 g. of IV in 10 cc. of glacial acetic acid and 10 cc. of water and boiling with 5 g. of zinc dust for 12 minutes. The mixture is cooled, filtered and the filtrate precipitated by the addition of ice-water (3 g.). The crude product is recrystallized from petroleum ether and washed with benzine, m.p. 72–74°. The m.p. of a mixture of this substance and the product of the bromination of resorcinol monomethyl ether is not depressed. The methylation of this substance yields 4,6-dibromoresorcinol dimethyl ether, m.p. 141–143°.[1]

536 WEST 113 ST.
NEW YORK 25, N. Y.   RECEIVED JULY 6, 1951

Ultrasonic Velocity in Some Alkyl Aryl Ketones

BY R. T. LAGEMANN,[1] B. F. LANDRUM,[2] C. T. LESTER,
O. MILNER AND E. G. McLEROY

The results to be described represent further efforts to find what relationships exist between molecular structure and the velocity of ultrasonic waves in liquids. Previous work has been reviewed by several writers,[3-5] including a recent paper by two of the present authors.[6]

The fifteen alkyl aryl ketones investigated are listed in Table I. An examination of Table I shows that increase in molecular weight is accompanied by a decrease in ultrasonic velocity within the limits of this series. When increase in molecular weight is accompanied by chain branching a considerably greater drop in velocity is noted. A similar effect of chain branching has been noted in isomeric alcohols.[7] When the molecular sound velocity[8] of these ketones are computed, the most highly branched ketones also show the lowest values within any group of isomers.

Experimental[9]

Preparation of Ketones.—The acetophenones, propiophenones and isobutyrophenones were prepared by a standard procedure.[10] The pivalophenones were prepared by the procedure of Marvel and co-workers.[11] All the ketones were twice distilled through an efficient column. Constant boil-

(1) M. Kohn and G. Loeff, *Monatsh.*, **45**, 590 (1924).

(2) M. Kohn and G. Loeff, *ibid.*, **45**, 594 (1924).

(3) L. Raiford and J. H. Scott, *J. Org. Chem.*, **2**, 213 (1937).

(4) H. Hodgson and R. C. Dyson *J. Chem. Soc.*, 946 (1935).

(5) M. Kohn and L. Steiner, *J. Org. Chem.*, **12**, 30 (1947).

(1) Physics Dept., Vanderbilt University, Nashville, Tennessee.

(2) Taken in part from the Ph.D. Thesis of B. F. Landrum, Emory University, 1951.

(3) S. Parthasarathy, *Current Science*, **6**, 322 (1938).

(4) L. Bergman, "Der Ultraschall," S. Hirzel, Zurich, 1949.

(5) P. Vigoureux, "Ultrasonics," John Wiley and Sons, Inc., New York, N. Y., 1951.

(6) R. T. Lagemann, R. Gwin, C. T. Lester, J. R. Profitt, Jr., and E. C. Suratt, THIS JOURNAL, **73**, 3212 (1951).

(7) A. Weissler, *ibid.*, **70**, 1634 (1948).

(8) M. R. Rao, *J. Chem. Phys.*, **9**, 692 (1941).

(9) All m.ps. and b.ps. reported are uncorrected.

(10) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 3.

(11) J. H. Ford, C. D. Thompson and C. S. Marvel, THIS JOURNAL, **57**, 2619 (1935).

TABLE I

ALKYL ARYL KETONES

4-R	B.p. °C.	B.p. Mm.	$n^{30}D$	d^{30}	V_{10}	Veloc., m./sec. V_{20}	V_{30}	Mol. sound veloc. at 30°	Ad. comp., dynes cm.² at 30° × 10¹²
A. 4-R-Acetophenones									
H	100	12	1.5280	1.0193	1537[p]	1502[p]	1463[p]	1338	45.9[p]
Me[a,b]	70	3	1.5303	0.9966	1532	1495	1457	1526	47.2
Et[a,c]	89	3	1.5252	.9849	1526	1487	1453	1704	48.1
Isoprop[d]	109	3	1.5187	.9705	1503	1467	1429	1883	50.5
t-Bu[e]	112	2	1.5168	.9574	1499	1464	1427	2073	51.3
B. 4-R-Propiophenones									
H	90	3	1.5212	1.0014	..	1493[p]	1456[p]	1519	47.1[p]
Me[f]	100	3	1.5238	0.9831	1525	1486	1450	1706	48.4
Et[a,g]	108	3	1.5199	.9704	1517	1481	1444	1889	49.4
Isoprop[h]	125	3	1.5141	.9560	1498	1460	1424	2074	51.6
t-Bu[i]	162	5	1.5138	.9495	1493	1457	1420	2252	52.2
C. 4-R-Isobutyrophenones									
H[j]	107	3	1.5134	0.9747	1486	1448	1408	1704	51.8
Me[k]	119	4	1.5147	.9605	1484	1448	1410	1894	52.4
Et[l]	122	3	1.5126	.9510	1484	1445	1411	2079	52.8
Isoprop[m]	126	2	1.5079	.9383	1474	1433	1399	2268	54.4
t-Bu[n]	132	2	1.5072	.9361	1470	1432	1395	2439	54.9
D. 4-R-Pivalophenones									
H[o]	71	2	1.5057	.9612	1461	1423	1383	1880	54.4
Me[o]	77	2	1.5066	.9486	1461	1425	1387	2072	54.8

[a] A. Klages and G. Lickroth, *Ber.*, **32**, 1558 (1899). [b] M.p., semicarbazone, 205°. [c] M.p., semicarbazone, 196°. [d] O. Widman, *Ber.*, **21**, 2225 (1888); m.p., semicarbazone, 203°. [e] G. F. Hennion and S. F. deC. McLeese, THIS JOURNAL, **64**, 2421 (1942); m.p., semicarbazone, 230°. [f] A. Klages, *Ber.*, **35**, 2252 (1902); m.p., semicarbazone, 188°. [g] M.p., semicarbazone, 151°. [h] *Anal.* Calcd.: C, 81.77; H, 9.15. Found: C, 82.07; H, 9.24; m.p., semicarbazone, 158°. [i] H. A. Bruson and O. Stein, *C. A.*, **29**, 4773 (1935); m.p. semicarbazone, 200°. [j] A. Lapworth and V. Steele, *J. Chem. Soc.*, **99**, 1883 (1911); m.p. semicarbazone, 181°. [k] K. V. Auwers, *Ann.*, **408**, 244 (1915); m.p., semicarbazone, 102°. [l] *Anal.* Calcd.: C, 81.77; H, 9.15. Found: C, 81.89; H, 9.40; m.p., semicarbazone, 105°. [m] *Anal.* Calcd.: C, 82.10; H, 9.47. Found: C, 81.84; H, 9.58; m.p., semicarbazone, 107°. [n] G. F. Hennion and L. A. Auspos, THIS JOURNAL, **65**, 1603 (1943); m.p., semicarbazone, 116°. [o] D. E. Pearson, *ibid.*, **72**, 4169 (1950). [p] Previously determined, *cf.* ref. 6.

ing, constant index center cuts were used in the determinations of physical properties listed in Table I.[12] Acetophenone and propiophenone were purchased from Matheson Co. and are included for comparison.

Measurement of Velocity.—The ultrasonic velocity of the liquids was measured by use of a variable–path ultrasonic interferometer[13] which employs a piezo-electric quartz crystal driven at 500 kc. per second by a crystal-controlled oscillator. All measurements were made with the interferometer submerged in a constant temperature water-bath.

Acknowledgment.—We wish to thank R. E. Donaldson, Dr. D. R. McMillan and A. E. Robinson for their help on this problem. One of us (R. T. L.) wishes to acknowledge a grant from the Research Corporation.

(12) The expense of ketone synthesis was borne by a contract from the Office of Naval Research. The rates of oximation of all but the last two have been reported, *cf.* M. J. Craft, B. F. Landrum, E. C. Suratt and C. T. Lester, THIS JOURNAL, **73**, 4462 (1951).

(13) D. R. McMillan, Jr., and R. T. Lagemann, *J. Acoust. Soc. Am.*, **19**, 956 (1947).

DEPARTMENT OF CHEMISTRY
EMORY UNIVERSITY
EMORY UNIVERSITY, GEORGIA   RECEIVED AUGUST 16, 1951

The Behavior of Anthrone on Some Alumina Columns

BY J. H. PINCKARD, A. CHATTERJEE AND L. ZECHMEISTER

When a benzene solution of pure, pale-yellow anthrone is adsorbed from benzene on a suitable alumina–celite column, a colored heterogeneous zone appears within a few minutes. When, subsequently, this adsorbate is washed with large volumes of benzene, the colored zone is resolved and some of its components migrate slowly downwards while much larger quantities of a colorless and non-fluorescent substance runs through the column. The latter substance is, however, not anthrone but anthraquinone. Under the conditions applied the yield varies between 80–90%. In contrast, a mixture of roughly equal parts of anthrone and anthraquinone is obtained in the washings if an "acid" brand of alumina is applied. A celite column has no effect on anthrone.

Experimental

One gram of vacuum-sublimed analytically pure anthrone (Calcd. for $C_{14}H_{10}O$: C, 86.57; H, 5.19. Found: C, 86.71; H, 5.12; m.p. 154–158°, cor.) which according to spectroscopic tests did not contain any anthraquinone, was dissolved in 100 ml. of benzene and poured, with suction, onto a 24 × 4.2 cm. alumina celite column (4:1). (Activated alumina "Alorco," Grade F, −80 mesh, reground to −200 mesh; Celite No. 545, Johns–Manville.) About a 2 cm. broad, brownish-yellow zone appeared near the top which during the subsequent development by means of 8 liters of benzene was resolved into a narrower, very strongly adsorbed brownish-red zone and a pale yellow substance with greenish fluorescence in ultraviolet light. This substance was present in small amounts only and spread over the rest of the adsorbent; only traces of it reached the chromatographic filtrate.

The main product of the conversion, *i.e.*, anthraquinone, ran through much more easily and could be collected from the filtrate. While passing through the column, it quenched