

## PREPARATION OF SOME ALKYL ARYL CARBINOLS AS INTERMEDIATES OF BHILAWANOL TYPE COMPOUNDS

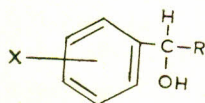
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The Grignard reaction of *o*-, or *m*-, or *p*-methoxybenzaldehyde with a straight chain, saturated alkyl halide, having C<sub>11</sub> to C<sub>17</sub> carbon atoms has led to the preparation of a large number of alkyl methoxyphenyl carbinols. These carbinols can be converted into compounds analogous to bhilawanol by dehydration and demethylation.

Because of the physiological properties of the phenolic compounds isolated from *Semecarpus anacardium* and *Rhus vernicefera*<sup>1</sup> it was considered of interest to investigate the possibility of synthesizing these compounds by preparing their analogues. The chemical and physiological characteristics of these analogues are proposed to be studied at a later stage. A series of model compounds having the following general structure have been synthesized.



where R=C<sub>11</sub>H<sub>23</sub>-C<sub>17</sub>H<sub>35</sub>, and X=OCH<sub>3</sub> at the *o*-, or *m*-, or *p*-position. The synthesis or study of such compounds has so far not been reported in the literature.

The first series in these model compounds consisted of alkyl methoxyphenyl carbinols which may be converted to hydroxyphenalkylenes of the type as are present in the *Semecarpus anacardium* extract. These can further be hydrogenated to the type of compound, analogous to tetrahydro-urushiol.

The compounds mentioned in the present study have involved Grignard synthesis in which the requisite methoxybenzaldehyde has been reacted with an alkyl magnesium halide having the desired number of carbon atoms in the alkyl group. The benzaldehydes employed were *o*-, *m*-, and *p*-substituted whereas the alkyl halides used had a saturated chain length of C<sub>11</sub> to C<sub>17</sub> carbon atoms.

### Experimental

All m.p.s were determined on a Kofler block and are uncorrected. The yields given here refer to the mean value of at least two experiments. Since the halides and the methoxy-substituted benzaldehydes were not available they were pre-

pared in the laboratory. All extracts were dried over sodium sulphate.

*o*-Methoxy benzaldehyde,<sup>2</sup> *m*-methoxy benzaldehyde<sup>3</sup> and *p*-methoxy benzaldehyde<sup>4</sup> were prepared as described in the literature in 68%, 78% and 54% yields, respectively. The pure compounds had the same b.p.s and refractive indices as reported in the literature. All the bromides used in this study, except for the 1-bromotetradecane, were prepared from the corresponding acids by the general procedure described by Cristol.<sup>5</sup> 1-Bromotetradecane, however, was prepared from *n*-tetradecanol according to the instructions of Vogel<sup>6</sup> in 69% yield. The other bromides were obtained in the following yields and had the same physical constants as reported in the literature:

1-Bromoundecane<sup>7</sup> (60%), 1-bromotridecane<sup>8</sup> (63%),  
1-bromopentadecane<sup>9</sup> (65%), 1-bromoheptadecane<sup>10</sup> (66%),  
1-bromododecane<sup>11-12</sup> (88%), and 1-bromohexadecane<sup>13</sup> (75%).

*Condensation of the Aldehyde with the Alkyl Halides.*—The Grignard reagent was prepared by reacting equimolecular (0.15 mole) amounts of magnesium (in g-atoms) and the respective alkyl bromide in sodium-dry ether as usual. Solutions of equimolecular (0.15 mole) amount of *o*-, *m*-, and/or *p*-methoxy benzaldehyde in dry ether were added separately to the Grignard reagent with stirring over a period of about 1 hr. The reaction mixture was then treated with aqueous sulphuric acid (7%) till the aqueous lower layer became acidic. The ethereal layer was separated and washed with water. The solvent was removed and the residue was taken up in about 100 ml of 95% ethanol (95%). This ethanolic solution was then treated with a saturated aqueous solution of sodium bisulphite, that formed an adduct with the unreacted methoxy benzaldehyde. The addition product was removed by filtration and the filtrates were extracted with benzene and washed with

TABLE I.—PHYSICAL CONSTANTS AND COMBUSTION DATA OF *o*-, *m*-, AND *p*-ALKYL METHOXYPHENYL CARBINOLS.

Carbinol	Yield %	B.p. °C	M.p. °C	Refractive index	Required %		Found %	
					C	H	C	H
Undecyl <i>o</i> -methoxyphenyl	40	206–8°/4.5 mm	—	1.479	78.08	11.0	78.2	11.1
Undecyl <i>m</i> -methoxyphenyl	38	208–10°/4.5 mm	—	1.483	78.08	11.0	78.1	11.3
Undecyl <i>p</i> -methoxyphenyl	36	—	34–35°	1.484	78.08	11.0	78.1	11.2
Dodecyl <i>o</i> -methoxyphenyl	77	226–28°/3.5 mm	—	1.478	78.4	11.01	78.0	11.4
Dodecyl <i>m</i> -methoxyphenyl	70	236–38°/4.5 mm	—	1.480	78.4	11.1	78.3	11.0
Dodecyl <i>p</i> -methoxyphenyl	77	—	40°	1.482	78.4	11.01	78.7	11.6
Tridecyl <i>o</i> -methoxyphenyl	38	236–38°/3.5 mm	—	1.478	78.75	11.25	78.9	11.3
Tridecyl <i>m</i> -methoxyphenyl	35	—	75°	1.479	78.75	11.25	79.2	11.4
Tridecyl <i>p</i> -methoxyphenyl	37	—	54–65°	1.481	78.75	11.25	79.0	11.4
Tetradecyl <i>o</i> -methoxyphenyl	73	—	45°	1.477	79.04	11.37	78.7	11.2
Tetradecyl <i>m</i> -methoxyphenyl	74	—	42°	1.478	79.04	11.37	78.7	11.6
Tetradecyl <i>p</i> -methoxyphenyl	76	—	52°	1.479	79.04	11.37	79.0	11.1
Pentadecyl <i>o</i> -methoxyphenyl	35	—	45°	1.475	79.3	11.5	78.8	11.6
Pentadecyl <i>m</i> -methoxyphenyl	38	—	46°	1.477	79.3	11.5	79.3	11.8
Pentadecyl <i>p</i> -methoxyphenyl	37	—	67°	1.478	79.3	11.5	79.3	11.6
Hexadecyl <i>o</i> -methoxyphenyl	63	—	52°	1.474	79.5	11.6	79.6	11.8
Hexadecyl <i>m</i> -methoxyphenyl	63	—	47°	1.475	79.5	11.6	79.6	12.0
Hexadecyl <i>p</i> -methoxyphenyl	72	—	50–51°	1.476	79.5	11.6	79.4	11.9
Heptadecyl <i>o</i> -methoxyphenyl	45	—	39.5°	1.473	79.8	11.7	79.0	11.0
Heptadecyl <i>m</i> -methoxyphenyl	47	—	53.5°	1.474	79.8	11.7	79.4	11.5
Heptadecyl <i>p</i> -methoxyphenyl	44	—	73–74	1.475	79.8	11.7	79.9	12.0

water. The extracts were dried and filtered. The solvent was removed from the filtrate by distillation. The residues were then either distilled under reduced pressure or crystallised to constant m.p. from light petroleum (b.p. 40–60°). A list of the *o*-, *m*-, and *p*-alkyl methoxyphenyl carbinols thus prepared, along with some of other physical constants and combustion data, is given in Table I.

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