

which shows a markedly broadened band at  $\sim 3340\text{ cm}^{-1}$  and a considerable shift in the absorption of the carbonyl band, with a maximum at  $1674\text{ cm}^{-1}$ .

It is of interest that the infrared spectrum of gelsemicine itself in Nujol mull shows a double peak in the carbonyl region, whereas a single maximum is obtained in chloroform solution (Fig. 3). It seems that the  $\text{C}=\text{O}$  group, only in some, but not all molecules of the crystalline gelsemicine, is involved in the hydrogen-bond formation. The  $\text{C}=\text{O}$  bond in the spectrum in chloroform solution lies between the position of the two peaks of the Nujol mull spectrum and this indicates that the  $\text{C}=\text{O}$  groups of all the molecules may be involved in H bonding with the  $\text{C}-\text{H}$  group of chloroform. Although crystalline gelsemicine itself has not been X-ray analyzed, some support to this explanation is given by the fact that in gelsemicine hydrobromide hemihydrate, N-methyl-gelsemicine hydrobromide tetrahydrate (6), and also in N-methyl-gelsemicine hydriodide of space group  $P2_1$ , the asymmetric unit was found to consist of two molecules which are, therefore, crystallographically not equivalent. This tendency of the compound to crystallize in pairs of molecules may well be due to the shape of its skeleton which contains a large planar oxindole group. In this connection, it is noteworthy that the infrared spectrum of dihydrogelsemine in chloroform also shows a single peak in the carbonyl region, although in a mull, a double peak is obtained.

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#### THE CLEAVAGE OF ETHERS BY *t*-BUTYLMAGNESIUM BROMIDE AND COBALTOUS CHLORIDE<sup>1</sup>

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In connection with attempts to break ether bonds in wood lignins by mild methods, the effect of the above Grignard-cobaltous chloride reagent on 2-methoxydiphenyl ether was briefly studied. Kharasch and Huang (1) discovered that the addition of anhydrous cobaltous chloride enabled a Grignard reagent to cleave many diaryl and benzyl aryl ethers to a mixture of the corresponding hydrocarbon and phenol in 3 to 4

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hours at 36°, instead of in 15 to 18 hours at 180–200°. No scission of methyl phenyl and ethyl phenyl ethers was observed. *n*-Butylmagnesium bromide was effective (1, 2), but Tomita and Watanabe (3) found that the yield of cleavage products was somewhat greater when the tertiary isomer was used; the replacement of diethyl ether by tetrahydrofuran as the solvent increased the yield threefold.

On the present occasion, eight experiments with 2-methoxydiphenyl ether were carried out, the Grignard reagent being made from either *n*-butyl or *t*-butyl bromide, and the solvent being ether or tetrahydrofuran. The best result was obtained with *t*-butylmagnesium bromide in tetrahydrofuran. With a 30-fold molar excess, 36% of the original substance was recovered unchanged together with 35% of phenols, corresponding to a degree of cleavage of about 60%. This yield corresponded closely to the value of 62% obtained by Tomita and Watanabe (3) for the same compound. Both guaiacol and phenol were isolated as the pure, crystalline benzoates, and cleavage therefore occurred on both sides of the diphenyl ether oxygen atom, in agreement with the work of Kharasch and Huang (1). Tomita and Watanabe (3) thought that this ether oxygen atom was completely retained by the guaiacol (benzene presumably was the only other product), but an attempt to repeat their isolation of the guaiacol as the *p*-nitrobenzoate gave a crystalline product which probably contained some of the phenol derivative. Fruitless attempts were also made to detect catechol, by paper chromatography, among the products, and this negative result agreed with the claim that methyl phenyl ether groups were not affected by the reagent.

*t*-Butylmagnesium bromide – cobaltous chloride, when warmed with a suspension of fully methylated spruce formaldehyde periodate lignin (4) in tetrahydrofuran, produced 2% of phenolic material which resinified too rapidly to be examined in detail, together with a little neutral, high-boiling oil. There was no clear evidence that any cleavage of ether groups occurred in this lignin. When the experiment was repeated with fully methylated spruce periodate lignin, the resulting 4% of ether-soluble material probably contained guaiacol, and the 90% of residual lignin increased in methoxyl content from 17.2 to 18.5% on remethylation with diazomethane. In this case, about 0.7% of phenolic groups might have been liberated by cleavage.

## EXPERIMENTAL

### Materials

Tetrahydrofuran, boiling correctly at 76°, was used not more than 2 days after purification by distillation in succession from solid sodium hydroxide, metallic sodium, and lithium aluminum hydride. The Grignard reagent was made from pure *t*-butyl bromide and dry, polished magnesium ribbon (5, 6); the use of powdered crystals of sublimed magnesium, obtained through the courtesy of Dow Chemical Company of Canada, yielded a particularly clear, colorless reagent (7). Dilution of an aliquot with a known volume of standard acid, and a back titration with standard alkali to a phenolphthalein end point (8), established the molarity of the reagent. The yield amounted to 50% of the magnesium when tetrahydrofuran was the solvent, whereas the reported yield was 33% (6).

A published method (9) of preparing anhydrous cobaltous chloride was modified by heating the pure hexahydrate for 2 days at 45° and 20 mm pressure, and then gradually raising the temperature to 220° (1 mm). The light pink of the partly dehydrated product changed through dark blue to the pale blue color of the anhydrous salt, which was

extremely finely divided. Ullmann and Stein's method (10) was used to synthesize 2-methoxydiphenyl ether, which was recrystallized from hexane and redistilled under diminished pressure; m.p.  $76^{\circ}$ , the recorded value being  $78^{\circ}$ .

#### *Cleavage of 2-Methoxydiphenyl Ether*

The apparatus consisted of a three-necked flask equipped with ground-glass joints, a magnetic stirrer, a reflux condenser, leads for dry nitrogen gas, and an L-shaped tube, revolving in a ground-glass joint, for the addition of the anhydrous cobaltous chloride. This tube could be warmed externally to prevent the condensation of solvent, which made the finely divided chloride sticky. A solution of 0.098 mole of *t*-butylmagnesium bromide in tetrahydrofuran was filtered through dry glass wool into the flask, the volume plus rinsings being 80 ml. After 1.3 g (6.5 mmoles) of 2-methoxydiphenyl ether had been added, the apparatus was flushed with nitrogen, and solution was completed by gentle heating and stirring. The cobaltous chloride, 4.68 g (36 mmoles), was then added from the L tube in 12 successive portions at 15-minute intervals, after which the mixture was heated for 3 hours under reflux.

The mixture was acidified near  $0^{\circ}$  with 4 *N* hydrochloric acid and thoroughly extracted with ether, and the extract was re-extracted with 5% aqueous sodium hydroxide (1). A neutral fraction, 0.50 g, isolated from the ether, yielded 0.375 g (29%) of twice-recrystallized 2-methoxydiphenyl ether with the correct melting point and mixed melting point. Benzoylation (5) of the product extracted by the alkali, 0.50 g, yielded 0.72 g of crystals, m.p.  $51-56^{\circ}$ , which on recrystallization from ethanol produced 0.45 g of guaiacol benzoate, m.p.  $57-58^{\circ}$ , and mixed m.p.  $56-58^{\circ}$ . Evaporation of the ethanol mother liquors left a gum which on standing deposited 0.07 g (0.35 mmole) or 5% of crystals melting at  $63-66^{\circ}$ , increased to m.p.  $69^{\circ}$  by recrystallization. Authentic phenyl benzoate had this melting point, and a mixed melting point with the crystals was not depressed. A further 0.08 g of pure guaiacol benzoate, isolated from the final mother liquors, brought the total yield of this product to 2.3 mmoles or to 35% of theory. Since a control benzoylation of pure guaiacol gave only a 50% yield of the pure, recrystallized benzoate, the yield of guaiacol actually produced in the cleavage was probably near 70%.

In another experiment, a small portion of the alkali-soluble product from the scission of 1.04 g (5.2 mmoles) of 2-methoxydiphenyl ether was chromatographed on paper for 20 hours with butanol - 2% aqueous ammonia as the solvent and a ferric chloride mixture (4) as the spray. Only the spot characteristic of guaiacol,  $R_f$  0.95, was present, and there was no spot in the catechol position,  $R_f$  0.87. The remainder of the product, when esterified with *p*-nitrobenzoyl chloride in pyridine (5), yielded 0.47 g of material which was recrystallized once from ethanol. Although the crystals, 0.26 g, melted rather sharply at  $96-97^{\circ}$ , many recrystallizations from ethanol and methanol separated them into 0.15 g melting at  $86-92^{\circ}$ , and 0.03 g melting at  $98-100^{\circ}$ . Since the melting points of the *p*-nitrobenzoates of guaiacol and phenol were  $97^{\circ}$  and  $102^{\circ}$ , respectively, the above product was probably an incompletely resolved mixture of these two compounds.

#### *Attempted Scission of Fully Methylated Lignins*

A 1.4-g sample of dry, finely divided spruce formaldehyde periodate lignin, fully methylated to  $\text{OCH}_3$ , 15.0% (4), was suspended in 90 ml of tetrahydrofuran containing 80 mmoles of *t*-butylmagnesium chloride. Six grams of anhydrous cobaltous chloride was added in 12 portions during 3 hours, and the subsequent heating under reflux was for 3 hours. The cold, acidified suspension was then extracted with ether, and the aqueous

residue was dialyzed against distilled water. The non-dialyzed portion yielded 1.20 g of a precipitate. Found: ash, 0.7%;  $\text{OCH}_3$ , 12.5%, not altered by methylation with diazomethane. The ether extract contained 0.2 g of a neutral, high-boiling oil, and 0.03 g of alkali-soluble material with  $R_f$  0.21 on paper chromatograms.

The experiment was repeated with 1.42 g of spruce periodate lignin fully methylated to  $\text{OCH}_3$ , 17.6; ash, 1.2% (4). Dialysis of the aqueous portion of the reaction mixture yielded 1.29 g of insoluble material. Found: ash, 0.2%;  $\text{OCH}_3$ , 17.2%, increased to 18.6% by remethylation with diazomethane. The neutral ether-soluble oil, 0.085 g, was volatile enough to leave only 0.02 g of residue when heated at  $100^\circ$  *in vacuo*. When the ether-soluble phenols, 0.06 g, were chromatographed on paper only the spot of  $R_f$  0.95 pertaining to guaiacol was observed.

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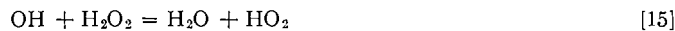
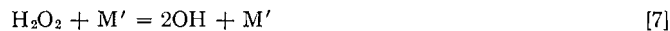
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### THE DECOMPOSITION OF HYDROGEN PEROXIDE IN THE PRESENCE OF HYDROGEN

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In a paper (1) presented at the Eighth International Combustion Symposium at Pasadena in September 1960, we reported a marked acceleration of the decomposition of  $\text{H}_2\text{O}_2$  in the presence of  $\text{H}_2$ . The studies were carried out using a flow system at atmospheric pressure, the partial pressure of  $\text{H}_2\text{O}_2$  varying from 0.2–1.0 mm Hg, and the partial pressure of  $\text{H}_2$  varying from 10–760 mm Hg. In such a system, where the  $\text{H}_2/\text{H}_2\text{O}_2$  ratios were relatively high, the experimental results are interpreted precisely by the following simple scheme:‡



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‡The numbering scheme is that used in earlier papers.