A Study on Alkylation of Phenol With Isano Oil

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Abstract

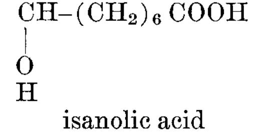
Phenol was alkylated with isano oil under both acidic and basic conditions. The products were studied with infrared and NMR spectroscopy. Both olefinic and acetylenic bonds apparently participated in the alkylation reactions. The phenol added 1,2 across these bonds mainly at the aromatic nucleus and predominantly in the ortho position. No vinyl ethers could be detected when KOH was used as the catalyst.

Introduction

Isano oil is a mixed fatty acid glyceride. The three fatty acids in this oil are: isanic (46%), isanolic (44%) and bolekoic (1) or bolekic (2) (9%). The structures of the first two were fully established (1,2). Both possess conjugated triple bonds:

$$H_2C = CH(CH_2)_4\,C \equiv C{-}C \equiv C{-}(CH_2)_7\,COOH$$

isanic acid



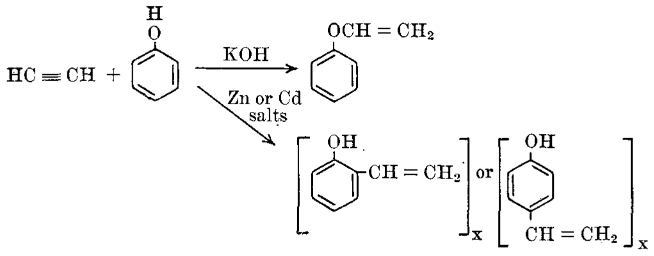
$$H_3C(CH_2)_2\,CH = CH{-}C \equiv C{-}C \equiv C{-}CH_2{-}\underset{\substack{|\\ O\\ H}}{CH}{-}(CH_2)_6\,COOH$$

isanolic acid

The structure of the third fatty acid is not yet fully known. Scher (3) reported this fatty acid is a conjugated mid-chain *cis*-ene-diyne octadecanoic acid.

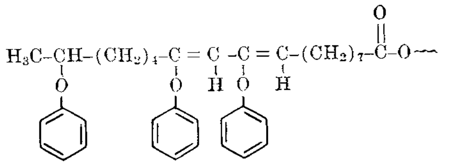
In a reaction of isano oil with phenols, the olefinic double bonds are expected to alkylate the phenolic moiety and the acetylenic portions of the molecules are also expected to add the phenol. Such reactions of phenols with triple bonds were reported to occur in both liquid and gaseous phases (4,5). These acetylenic reactions are catalyzed either by Friedel-Craft catalysts or by bases. The latter ones usually yield vinyl ethers while the former ones lead to vinylation of the phenolic nucleus.

Reppe suggested (4) that zinc and cadmium salts will initially yield vinyl ethers as well which subsequently rearrange similarly to the Claisen rearrangement.

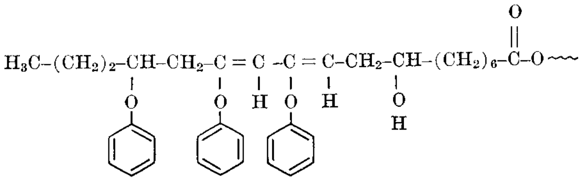


Mild Friedel-Craft catalysts and mild operating conditions can also yield ethers in the cases of olefinic alkylations of phenols (6). Furthermore, hydroxyl groups of the phenols complex with the catalysts. Nevertheless, it is generally accepted that ether formations need not necessarily occur as intermediate steps in such Friedel-Craft nuclear alkylations.

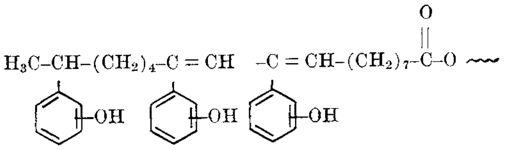
From the above considerations, additions of phenols to the isanic acid portions of the molecule could potentially lead to triethers:



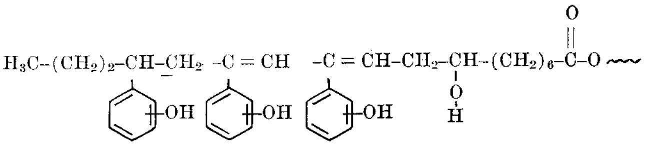
Similar triethers could be postulated for adducts of isanolic acids with phenols.



On the other hand, the phenols might actually be attached at the aromatic nucleus instead.



Adduct to isanic acid portion



Adduct to isanolic acid portion

As the bolekoic acid is apparently similar in structure to isanic and isanolic acids, similar adducts are expected. However, the products might actually contain both phenyl ethers and nuclear substituted phenols. Furthermore, such nuclear substitutions can be in the *para* and in the *ortho* positions.

In this study, an attempt was made to determine the structures of the products formed when different catalysts were employed with infrared spectroscopy and with nuclear magnetic resonance studies.

Experimental Procedures

A typical condensation reaction is shown in preparation of a condensate catalyzed by zinc chloride.

One hundred grams of isano oil were combined with 94 g of phenol and 20 g of freshly fused zinc chloride. The reaction mixture was then heated with stirring to 165 C for 5 hr. The brown product was washed twice with equal volumes of 5% Na_2CO_3 solution followed by two more washings with equal volumes of water. After that, the product was dissolved in 150 ml of *n*-butyl alcohol and dehydrated

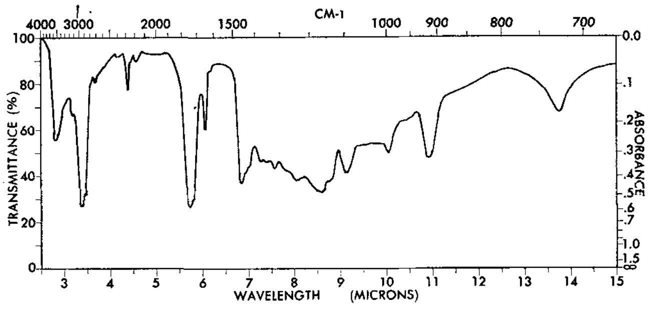


FIG. 1. Infrared spectrum of isano oil.

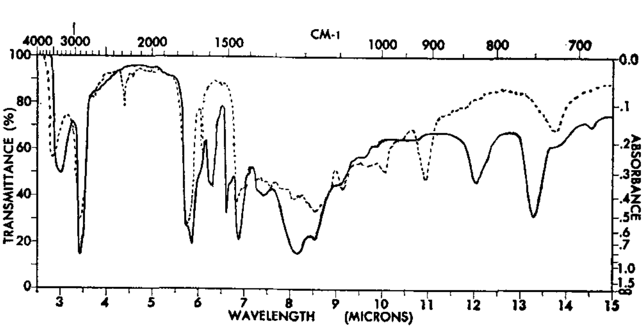


FIG. 2. Infrared spectrum of the reaction product of isano oil and phenol catalyzed by zinc chloride.

using azeotropic distillation. The remaining portion of the alcohol was then stripped with the aid of vacuum distillation. This left a brown tar which was dissolved in chloroform and chromatographed on a column of silicic acid, separating some small quantities of very dark tars from the main brown product. Condensation reactions catalyzed by H_2SO_4, zinc naphthenate and zinc formate were carried out in the same manner as with zinc chloride shown above.

Condensation Reactions Catalyzed by KOH

One hundred grams of phenol were combined with 28 g of KOH and 5 g of water and stirred at 90 C until all KOH dissolved. One hundred grams of isano oil were then added and the temperature raised to 185 C. This temperature and stirring were maintained for 10 hr. The product was then washed with dilute hydrochloric acid and then three times with water. Unreacted phenol and moisture were then removed by vacuum distillation. Hydrolytic cleavage of ether groups was carried out with 48% HBr solution in glacial acetic acid, according to established procedures (8).

Infrared spectra were obtained with the aid of Perkin-Elmer, Model 137, Infracord Spectrophotometer. The determinations were conducted on films deposited on NaCl plates. NMR spectroscopy was carried out on a Varian, Model 60, high resolution NMR Spectrometer using 60 megahertz. All determinations were carried out on solutions in deuterated chloroform. These were done at room temperature. The sweep width was 500 cps. The sweep offset was 100 cps.

Results and Discussion

Both acidic and basic catalysts were used. These were zinc chloride, sulfuric acid, zinc naphthenate, zinc formate and potassium hydroxide. The product from a zinc chloride catalyzed condensation was submitted to HBr in acetic acid hydrolysis in order to cleave ether groups.

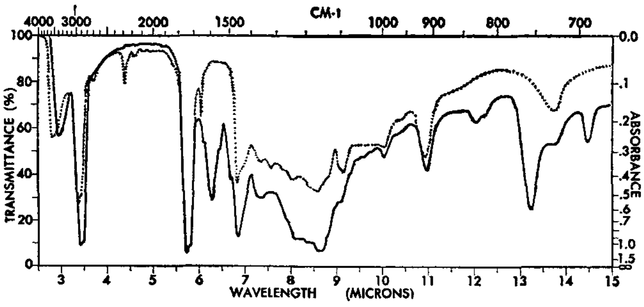


FIG. 3. Infrared spectrum of the reaction product of isano oil and phenol catalyzed by zinc formate.

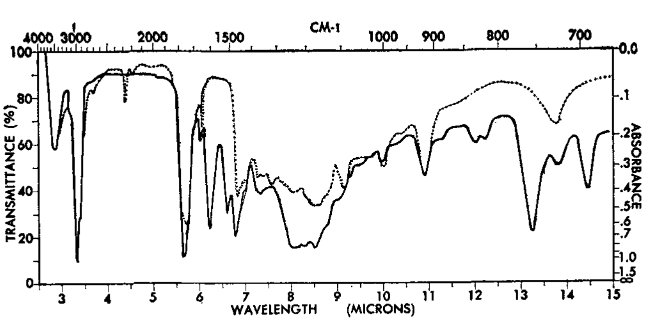


FIG. 4. Infrared spectrum of the reaction product of isano oil and phenol catalyzed by zinc naphthenate.

Infrared Spectra

Infrared spectra of the products are shown in Figures 2–6. The spectra of the parent compounds are indicated with dotted lines. The significant absorption peaks and the assignments of functional groups are summarized in Table I. Spectra of all products show disappearance of acetylenic linkage peaks at 4.35–4.40 μ as a result of the reaction. When zinc chloride and sulfuric acid catalysts were used, the vinyl unsaturation peaks (6) at 10.95 μ of the original isano oil (Fig. 1) disappeared. This absorption peak was due to the terminal double bond of isanic acid. Apparently, alkylation of phenol by this double bond proceeded to a high extent. However, when zinc salts of organic acid or when KOH were employed as catalysts, additions to this double bond were not as extensive because only some reduction in the 10.95 μ peak can be seen.

The alkaryl ethers usually exhibit strong absorption in the approximate region of 7.85–8.3 μ (6). However, when these are vinyl ethers, then the band location is uncertain (6). Also, the ester groups in the molecule can interfere. The infrared spectra of all the products indicate broadening from the original isano oil ester (C–O–C) absorption peak at 8.6–9.55 μ towards the longer wave length of the spectrum. In many cases, these become double peaks with the second absorption maximum at 7.85–8.3 μ. This indicates formation of some ether groups.

Infrared spectra of HBr hydrolysis product from the $ZnCl_2$ catalyzed condensate are shown in Figure 7. The above-mentioned ether peak at 7.85–8.3 μ is now absent. Apparently, some ether groups were present in the original condensate and were cleaved during hydrolysis (7).

The absorption peaks 11.9–12.05 μ, 13.3 μ and 14.5 μ are assigned to aromatic substitution (6). When zinc chloride or sulfuric acid were used to catalyze the reactions, the spectra of the products (Fig. 2 and 5) showed medium strength peaks for para-substituted aromatic structures, 11.9–12.05 μ. On the other hand, the use of zinc naphthenate zinc formate or KOH yielded products whose spectra showed only weak bands, indicating that fewer additions to phenol took place at the para positions.

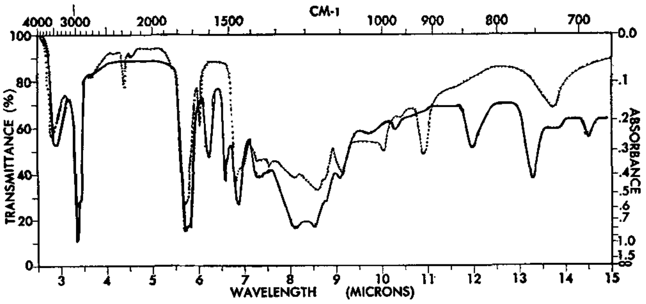


FIG. 5. Infrared spectrum of the reaction product of isano oil and phenol catalyzed by sulfuric acid.

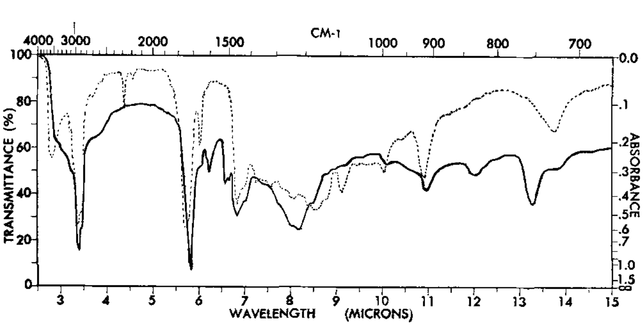


FIG. 6. Infrared spectrum of the reaction product of isano oil and phenol catalyzed by potassium hydroxide.

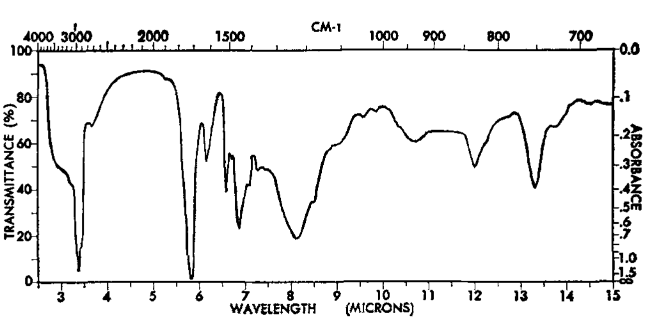


FIG. 7. Infrared spectrum of the HBr hydrolysate of the condensation product of phenol and isano oil catalyzed by zinc chloride.

The band assigned to ortho substitution is at 13.3 μ. The spectra of all products show strong bands in this region suggesting that alkylations occurred primarily ortho.

The peak at 14.5 μ is commonly associated with aromatic monosubstitution. Only the reactions of phenolic hydroxyl groups leading to ether formations would be expected to give rise to such absorptions. In the spectra of products from zinc chloride and sulfuric acid catalysis (Fig. 2 and 5) there are weak peaks at this region. Also, there are such peaks in the spectra of the products from zinc naphthenate and zinc formate catalysis but they are of medium intensity. However, it is interesting to note that infrared spectra of the product from KOH catalysis (Fig. 6) showed a complete absence of absorption in this region. This contradicts the literature (4) on reactions of acetylene and phenol catalyzed by KOH. We cannot explain it at this time.

Nuclear Magnetic Resonance

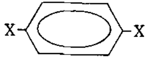
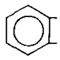
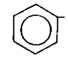
Figure 8 shows the NMR spectra of isano oil. Chemical shifts which can be attributed to the terminal methyl groups are at 0.92 ppm. The absorption position of the protons for chain methylene groups is at 1.40 ppm and that of the methylenic groups adjacent to carboxylic esters at 2.30 to 2.40 ppm. The chemical shift due to ester protons coming from the alcohol portions of the molecule is at 4.35 ppm. The absorption position at 5.05 to 6.28 ppm can be ascribed to internal olefins of isanolic acid. However, we are not able to associate any chemical shift with the OH group of isanolic acid.

Figure 9 shows the NMR spectra of the reaction product of isano oil and phenol catalyzed by zinc chloride. No significant changes can be seen in the chemical shift due to protons from CH_3 and from $(CH_2)_x$ groups. There is a new absorption position at 3.65–3.90 ppm which might be due to ether groups. There is also an increase in the amount of internal olefins as seen from an increase of chemical shifts at 5.5 ppm. However, there is no chemical shift at 4.95–4.05 ppm which was present in the original spectra of isano oil (Fig. 8). This signifies that the terminal double bonds disappeared as a result of the reaction. The absorption positions at 6.7 to 7.8 ppm are due to aromatic protons. They simply confirm further that phenol did add to the oil. The peak at 4.90 ppm is due to an OH chemical shift. This is confirmed from the spectra of sample with D_2O. Such an OH shift was not observed in the NMR spectra of isano oil (Fig. 8) and must therefore be a phenolic OH.

NMR spectra of the product from HBr hydrolysis (Fig. 10) of the above phenol adduct show some slight changes in the proton absorption due to methylene groups adjacent to the ester groups at 2.30 ppm. New peaks at 3.60–3.80 ppm are probably due to protons located on carbons attached to bromine atoms. What is much more significant, however, is that there does not appear to be any appreciable loss of aromatic protons judging from the peaks at 6.50 to 7.32 ppm. This suggests that the phenols were originally alkylated predominantly at the nucleus with only a minor quantity of ether groups having been formed. If this were not the case and if phenyl ethers formed predominantly, then HBr would have cleaved them and the quantity of aromatic protons would have been decreased drastically. The absorption position at 8.87 ppm is probably due to dimerized carboxyl groups. This is confirmed by the spectra of a sample containing D_2O. Such acid groups must be formed because HBr caused some hydrolytic attack on the ester linkages as well. The absence of internal double bonds in the molecule (5.05 to 6.0 ppm) suggests that HBr also saturated the olefin linkages.

The NMR spectra of the condensation product catalyzed by KOH are shown in Figure 11. It is interesting that here the chemical shifts due to ether groups at 3.65–3.90 ppm are not significant, judging by the integration of the area under the curve. This agrees with the information obtained from the infrared spectra. There is only a slight indication of any presence of terminal vinyl groups at 4.90 ppm. These spectra also show the presence of dimerized carboxyl groups seen from the chemical shift at 8.60 ppm and confirmed by D_2O spectra.

TABLE I
Summary of Significant Absorption Peaks from Infrared Spectra

Condensation catalyst	Absorption peaks							
	4.35–4.40 μ $C\equiv C$	6.35 μ $-C=C-$	6.65 μ $-C=C-\phi$	8.25 μ C–O–C	10.95 μ $-CH=CH_2$	11.9–12.05 μ 	13.3 μ 	14.5 μ 
$ZnCl_2$	Absent	Medium	Medium	Strong	Absent	Medium	Strong	Weak
Zinc naphthenate	Absent	Strong	Medium	Strong	Medium	Weak	Strong	Medium
Zinc formate	Absent	Strong	Medium	Strong	Medium	Weak	Strong	Medium
Sulfuric acid	Absent	Medium	Medium	Strong	Absent	Medium	Strong	Weak
KOH	Absent	Weak	Weak	Strong	Medium	Weak	Strong	Absent

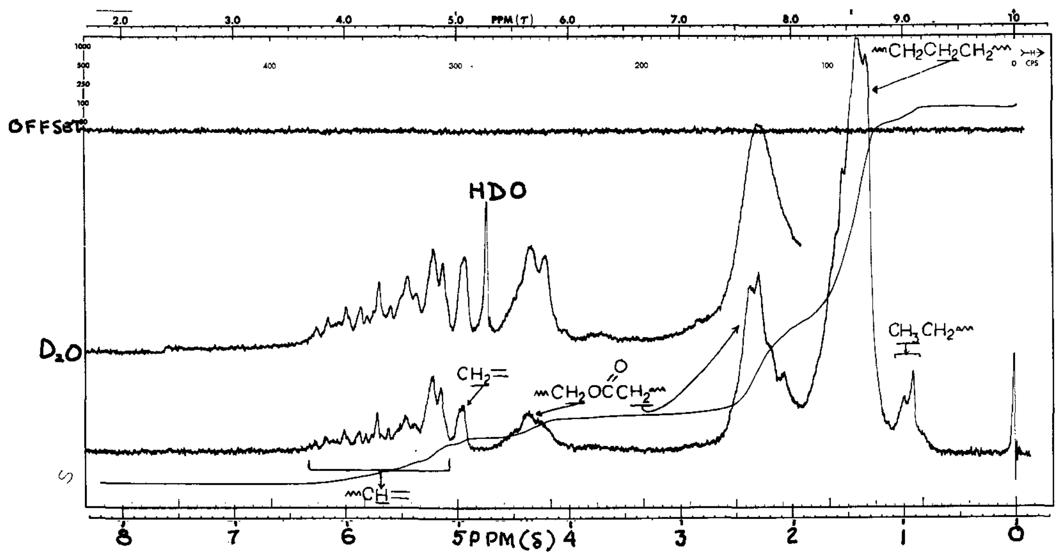


FIG. 8. NMR spectrum of isano oil.

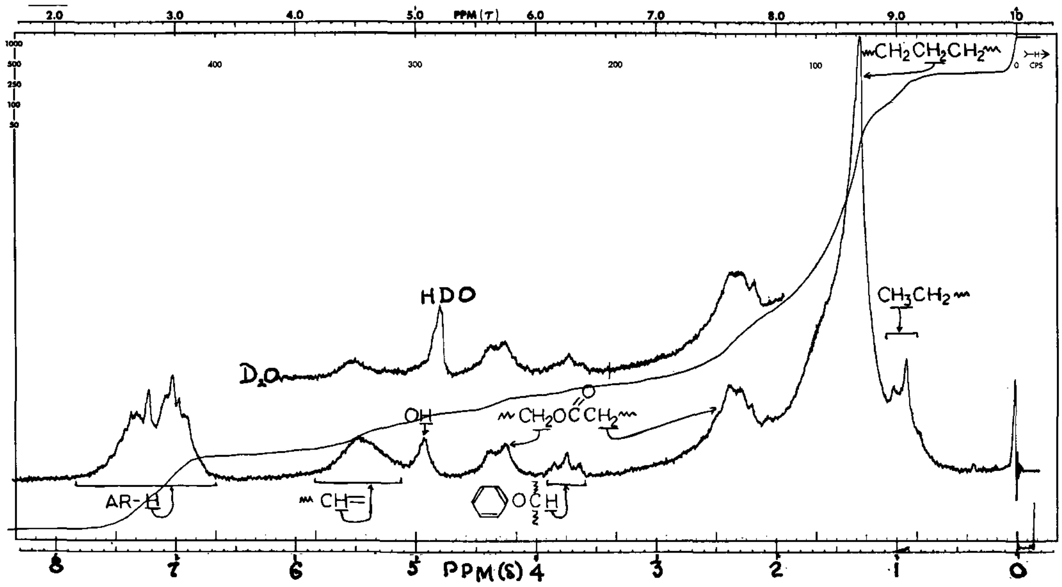


FIG. 9. NMR spectrum of the reaction product of phenol and isano oil catalyzed by zinc chloride.

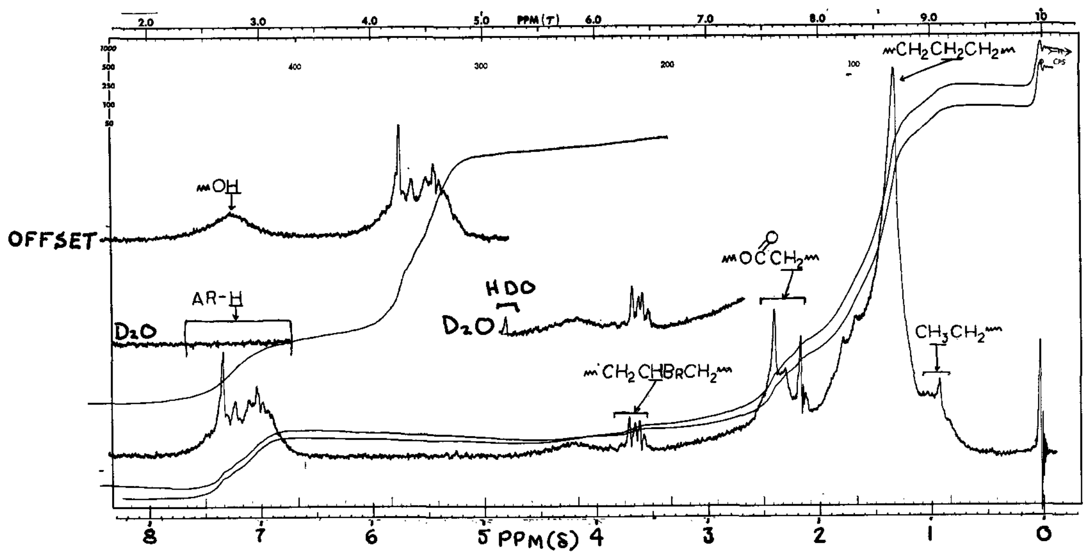


FIG. 10. NMR spectrum of the reaction product of isano oil and phenol catalyzed by potassium hydroxide and subsequently hydrolyzed by HBr.

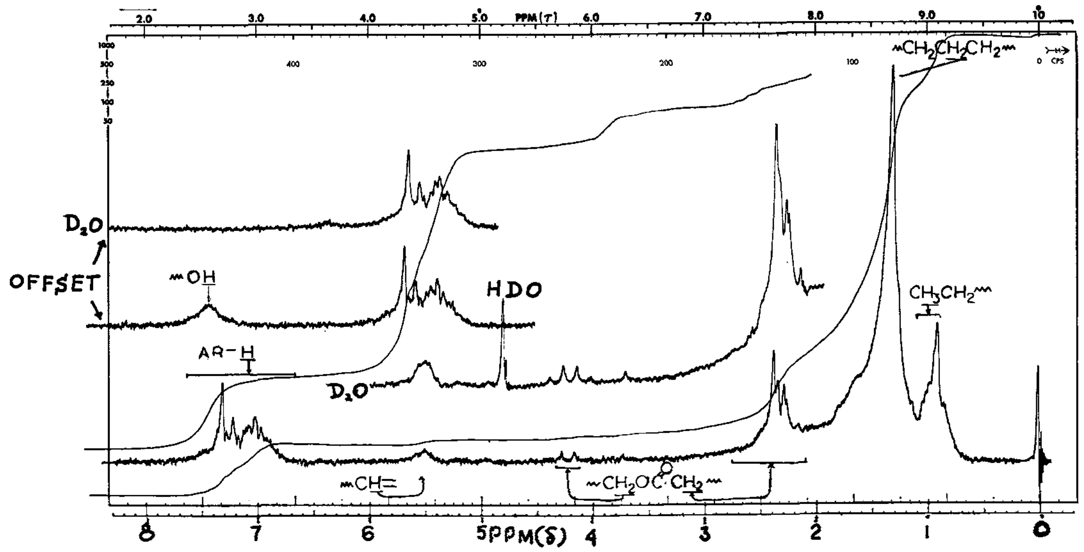
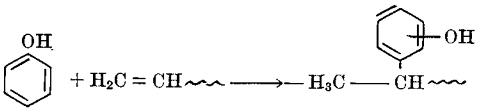


FIG. 11. NMR spectrum of the HBr hydrolysate of the reaction produced from isano oil and phenol catalyzed by zinc chloride.

By integrating the areas under the curves of NMR spectra shown in Figures 8, 9 and 11, we find that the original isano oil contained 18 methylene hydrogens for each methyl proton (coming from the terminal methyl groups). However, both reaction products possessed much lower ratios of methylene to methyl protons. Thus the zinc chloride-catalyzed reaction product (Fig. 9) had only 7 methylene hydrogens to each methyl hydrogen and the KOH-catalyzed product had only 5 methylene hydrogens to each methyl hydrogen. This indicates that the phenolic moiety in reacting with the terminal double bonds added predominantly at the penultimate carbons of isano oil acids in accordance with Markowinkoff's rule:



The above information is in agreement with that obtained from the infrared spectra (Fig. 6).

Conclusion

We conclude that: phenol was alkylated by both acetylenic and olefinic linkages in all reactions carried out; the alkylations of phenols were predominantly in the nuclear positions and mostly ortho to the hydroxyl groups; and only small amounts of aryl ethers formed with acidic catalysts and very little with KOH.

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