of *o*-nitrobenzoyl chloride. Our experience was similar. Small quantities appeared to distil satisfactorily, but this trouble was encountered in an 8-mole run. The volatile products ($POCl_3$, PCl_5) were removed at 100° (20 mm.), then the flask was equipped for vacuum distillation with an oil pump and a glas-col heating mantle. Before any distillate was collected the material detonated violently. Fortunately, however, there was a warning period of a few seconds.

Reasonably pure *o*-nitrobenzoyl chloride may be made without distillation by use of thionyl chloride instead of phosphorus pentachloride. The gaseous reaction products and any unused thionyl chloride were removed by aspirating with a stream of dry illuminating gas for a few hours.

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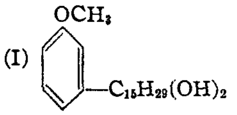
CASHEW NUT SHELL LIQUID. II. AN APPLICATION OF THE PREVOST REAGENT TO ALKENYL PHENOLS[1]

Sir:

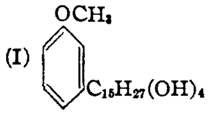
The noxious saps of numerous members of the *anacardiaceae* family, such as Poison Ivy, Cashew Nut Tree, Japanese Lac Tree, *etc.*, contain phenolic mixtures made up of saturated, mono-, di- and probably polyolefinic components. With the purpose of developing a method for separating and establishing the structures of such olefinic components, we have investigated the use of silver iodobenzoate.[2,3]

The monophenol, obtained by direct vacuum distillation of raw commercial cashew nut shell liquid, and possessing an average of two aliphatic double bonds,[1] was redistilled several times, methylated and then distilled. The resulting methyl ether possessed 1.56 double bonds. Treatment with silver iodobenzoate, and subsequent hydrolysis of the benzoates, yielded, on fractional crystallization from aqueous methanol, two crystalline glycols (A and B), both of which contained iodine. Both glycols showed no discoloration of bromine in carbon tetrachloride.

Glycol (A), m. p. 92–93°, analyzed correctly for an iodinated monoglycol.



(A)



(B)

Anal. Calcd. for $C_{22}H_{37}O_3I$: C, 55.35; H, 7.74; mol. wt., 476. Found: C, 55.55; H, 7.51; mol. wt. (ebulliometric in CCl_4), 478.

Glycol (B) m. p. 112–113° and analyzed correctly for an iodinated diglycol.

Anal. Calcd. for $C_{22}H_{37}O_5I$: C, 51.96; H, 7.28. Found: C, 51.92, 52.01; H,7.50, 7.43.

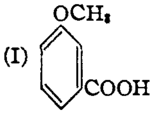
Oxidation of the mono glycol (A) with periodic acid in aqueous methanol gave *n*-heptaldehyde which was identified as the 2,4-dinitrophenylhydrazone, m. p. 106.5–107°, by mixed m. p. and analysis.

Anal. Calcd. for $C_{13}H_{18}O_4N_4$: C, 53.06; H, 6.12; N, 19.05. Found: C, 53.23; H, 6.21; N, 19.10.

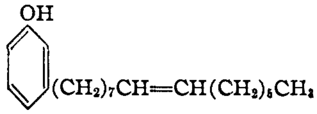
Oxidation of the mono glycol (A) with alkaline aqueous permanganate gave an aromatic acid containing iodine which analyzed correctly for (C).

Anal. Calcd. for $C_8H_7O_3I$: C, 34.54; H, 2.51. Found: C, 34.71; H, 2.77.

Catalytic hydrogenation of the mono glycol (A) using 5% Pd–$BaCO_3$ in ethanol yielded an iodine-free solid which is now under investigation.



(C)



Mono-olefinic component

The experiments described above establish that the mono phenol of commercial cashew nut shell liquid is a mixture of at least two different olefinic components: one a mono-olefin and the other a di-olefin. It appears likely that a more highly unsaturated component is also present. The mono-olefinic component is unsaturated in the 8–9 position of the side chain as established by the isolation of *n*-heptaldehyde after periodic acid oxidation of the glycol.

Further studies on the identification of the position of the iodine in the ring and the application of the Prevost reagent to the separation and identification of other unsaturated natural phenolic bodies, such as are found in poison ivy, are now in progress. Details of all this work will appear in forthcoming publications.

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[1] For the first article in this series, see Wasserman and Dawson, *Ind. Eng. Chem.*, **37**, 396 (1945).

[2] Prevost, *Comp. rend.*, **196**, 1129 (1933); **197**, 1661 (1933); **198**, 2264 (1934).

[3] Hershberg, *Helv. Chim. Acta.*, **17**, 351 (1934).

SELECTIVE DEMETHYLATION OF PARAFFIN HYDROCARBONS

Sir:

Paraffin hydrocarbons, as for example, pentane and hexane, are known to react in the presence of active hydrogenation catalysts, such as nickel, to produce primarily methane and carbon. Mixtures of hexane and hydrogen give methane as the major product at 400°.

We wish to record a new reaction, **the selective** demethylation of branched-chain paraffin **hydro-**

carbons by reaction with hydrogen, which results in the removal of *specific* methyl groups as methane and the formation of a paraffin having one less carbon atom. The methyl groups attached to secondary carbon atoms are removed much more readily than those attached to tertiary carbon atoms, while those bound to quaternary carbon atoms are the most stable.

The reaction may be carried out using nickel or cobalt catalysts with preferred temperatures ranging from 200–320° and pressures from atmospheric to 50 atmospheres. Careful control of reaction conditions at properly related values within these general ranges is essential. When conditions are so controlled, there is no carbon deposition, and the catalyst activity is maintained for long periods. Since the reaction products can undergo further demethylation to lower hydrocarbons, it is desirable to separate the reaction products after the conversion of the initial hydrocarbon has reached 30–40%.

Assuming no selectivity of demethylation, it is possible to calculate the theoretical product distribution based on the removal of a single methyl group. For example, of the three available methyl groups in isopentane, the removal of either one of the two attached to the tertiary carbon atom will lead to the formation of normal butane, while isobutane can be formed only by removing the methyl group attached to a secondary carbon atom. Actually, the selectivity of demethylation is so great that a striking difference is obtained between the calculated and actual product distributions. Thus, isopentane should yield 66.7% normal butane and 33.3% isobutane. However, the product of monodemethylation of this compound contained 8% normal butane and 92% isobutane. Similarly, neohexane should produce 75% isopentane and 25% neopentane, while actually the product contained only 6% isopentane and 94% neopentane. Monodemethylation of 2,2,3-trimethylpentane should give a product consisting of 60% 2,3-dimethylpentane, and 20% each of 2,2-dimethylpentane and 2,2,3-trimethylbutane. However, the experimental results showed the following distribution: 2,2,3-trimethylbutane 90%, 2,3-dimethylpentane 7%, and 2,2-dimethylpentane 3%.

A typical example of the demethylation of a paraffin hydrocarbon is given here; details of other experiments will be given in a forthcoming publication. A mixture of hydrogen and technical neohexane (90+% pure, Phillips) was passed over a nickel-on-kieselguhr catalyst[1] at 229° (catalyst temperature) and atmospheric pressure. The catalyst was heated in a stream of hydrogen at 538° for twelve hours prior to the experiment. The space velocity based on the hydrocarbon was 0.5 volume of liquid per volume of catalyst per hour. The molar ratio of hydrogen to hydrocarbon was 3.1 to 1. A total of 231 cc. of neohexane was passed over 100 cc. of catalyst in five hours. The liquid product, condensed at −78°, amounted to 92% of the charge. This material was subjected to a low-temperature fractionation to give the following major fractions:

Fraction	B. p. at 760 mm.	Mole %	Compound
2	−1 to +1°C.	4.3	*n*-Butane
4–7	7 to 11	36.8	Neopentane
9–12	27 to 36	1.7	iso- and *n*-pentane
15	42 to 53	53.1	Neohexane
1, 3, 8, 13, 14		4.1	Intermediate fractions

Fraction 6, b. p. 9° melted at −19° corresponding to a purity of 98+% neopentane [pure neopentane, b. p. 9.5° (uncor.), m. p. −16.6°[2]]. The presence of small amounts of normal pentane in the product is due to impurities present in technical neohexane.

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(1) V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

(2) F. D. Rossini, National Bureau of Standards, private communication.