

compound were similar to those of the monoacetate. An alcoholic solution of the substance gave a dark green coloration with a few drops of ferric chloride solution but showed no violet coloration on the subsequent addition of ammonia. The substance in glacial acetic acid solution gave a deep orange coloration on the addition of a few drops of concentrated sulfuric acid. The compound showed a negative Fehling's reduction and in pyridine solution it did not reduce Tollens' reagent. On acetylation of the *p*-toluenesulfonate derivative with sodium acetate and acetic anhydride, a product was obtained which no longer exhibited the green coloration with ferric chloride, but as the product could not be obtained in crystalline form it was not further investigated.

Anal. Calcd. for $C_{25}H_{22}O_3(OSO_2C_6H_4CH_3)_2$: C, 65.70; H, 5.09; S, 9.00; mol. wt., 712.8. Calcd. for $C_{25}H_{24}O_4(OSO_2C_6H_4CH_3)_2$: C, 64.1; H, 5.24; S, 8.77; mol. wt., 730.8. Found: C, 64.4; H, 5.08; S, 8.75; mol. wt. (Rast), 680, 650.

An amount of 200 mg. of the *p*-toluenesulfonate derivative was dissolved in 150 cc. of acetone and titrated directly with 0.1 *N* sodium hydroxide solution, using phenolphthalein indicator and the procedure described under the direct titration of osajin. The direct titer found was 2.65 cc. or 1.33 cc. of 0.1 *N* sodium hydroxide per 100 mg.; calcd. for one equivalent on $C_{25}H_{24}O_4(OSO_2C_6H_4CH_3)_2$: 1.37 cc.

Oxidation of Osajin.—Osajin (0.5 g.) was treated with 10 cc. of concentrated nitric acid. A vigorous reaction ensued, nitrogen dioxide was evolved and the color changed from yellow through brown to black, and then back to reddish-yellow. On concentration to near dryness, 0.16 g. of crystals was obtained which were identified as oxalic acid dihydrate (m. p. 98–99°; mixed m. p. unchanged; equivalent weight by titration, 70; calcd., 63; m. p. of oxal *p*-toluidide derivative, 266°; mixed m. p. unchanged).

Summary

1. A crystalline yellow substance has been isolated from the fruit of the osage orange (*Mac-lura pomifera* Raf.).

2. Two acetates and a *p*-toluenesulfonate of the above compound have been prepared in pure crystalline condition.

3. It is shown that the data on all the above compounds agree best with the formula $C_{25}H_{24}O_5$ as extended to $C_{24}H_{22}O(COO)(OH)_2$, for the naturally occurring substance. This formula is put forth provisionally and the name osajin is suggested for the compound.

COLUMBUS, OHIO

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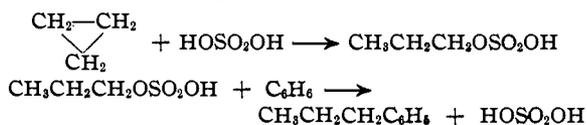
[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Alkylation of Benzene with Cycloparaffins in the Presence of Sulfuric Acid

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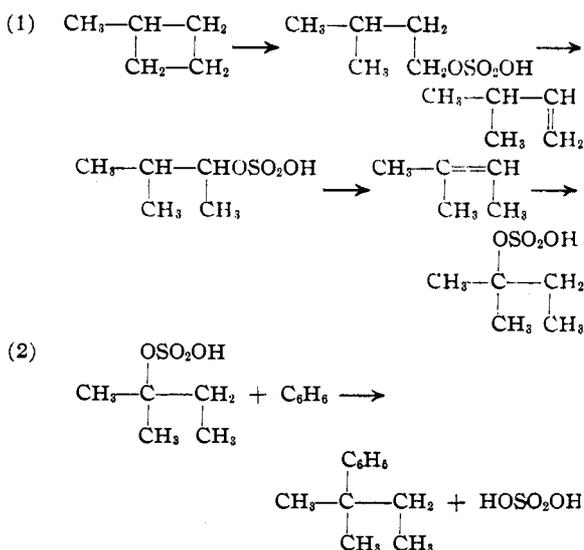
It is well known that the olefins alkylate benzene in the presence of sulfuric acid,¹ and since the lower cycloparaffins may be considered to contain a potential double bond, it was interesting to investigate whether they also could alkylate benzene under similar conditions.

Cyclopropane was found to alkylate benzene in the presence of cold sulfuric acid to yield *n*-propylbenzene, part of the cyclopropane being found in the catalyst acid in the form of *n*-propyl sulfate. Evidently, the cyclopropane did not first isomerize to propene,² in which case the alkylated product would have been isopropylbenzene. The reaction may be represented as follows.



The cyclobutane ring also alkylates benzene in the presence of cold sulfuric acid, *t*-amylbenzene be-

ing obtained from the interaction between methylcyclobutane and benzene. The formation of *t*-amylbenzene involves a rearrangement which can be visualized as follows.



(1) Ipatieff, Corson and Pines, *THIS JOURNAL*, **58**, 919 (1936).

(2) Ipatieff and Huhn, *Ber.*, **36**, 2014 (1903).

It is the sulfuric acid addition product of 2-methylbutene-2 which finally alkylates the benzene.

Another example of isomerization accompanying alkylation was previously observed by Ipatieff, Pines and Schmerling,³ who found that 2-methylbutene-3 alkylates benzene in the presence of sulfuric acid to give *t*-amylbenzene and not the expected 2-methyl-3-phenylbutane.

Cyclopentane also was tested under the same conditions but alkylation did not take place. Of the three cycloparaffins studied, cyclopropane was the most reactive.

Experimental

Cyclopropane, Benzene and Sulfuric Acid.—The cyclopropane was a pure commercial product. It boiled at -34 to -33° and did not react with alcoholic permanganate solution. Eighteen grams (0.43 mole) of cyclopropane was passed into a cold ($2-4^\circ$), stirred solution of 100 cc. (1.1 moles) of benzene and 25 cc. of 96% sulfuric acid. The time of addition was one hour. The hydrocarbon layer was separated and washed with cold 96% sulfuric acid, followed by water, dilute caustic, and water. Double distillation of the dried hydrocarbon mixture gave 6 g. of material boiling at $155-156.5^\circ$ which was identified as *n*-propylbenzene.⁴ Its diacetamino derivative was identical by mixed melting point with diacetamino-*n*-propylbenzene. The catalyst acid was diluted, made alkaline, and steam distilled. The distillate was saturated with potassium carbonate and extracted with ether. Three grams of *n*-propyl alcohol (b. p. $95-98^\circ$) was isolated from the latter, and identified by mixed melting point in the form of its 3,5-dinitrobenzoate.

Methylcyclobutane, Benzene and Sulfuric Acid.—Methylcyclobutane was prepared from pentaerythritol. Pentaerythritol was converted into its tetrabromide and the latter was debrominated by zinc dust.⁵ The resulting mixture of methylenecyclobutane and methylcyclobutene⁶ was hydrogenated with nickel catalyst at room temperature under an initial hydrogen pressure of 100 kg./sq. cm. The product (b. p. $35-35.5^\circ$ at 748 mm.; n_D^{20} 1.3866; d_4^{20} 0.688) did not decolorize alcoholic permanganate solution.

(3) Ipatieff, Pines and Schmerling, *THIS JOURNAL*, **60**, 353 (1938).

(4) Ipatieff and Schmerling, *ibid.*, **59**, 1056 (1937).

(5) Rave and Tollens, *Ann.*, **276**, 61 (1893); Gustavson, *J. prakt. Chem.*, [2] **54**, 93 (1896).

(6) Philipov, *J. prakt. Chem.*, **93**, 102 (1916).

Anal. Calcd. for C_4H_{10} : C, 85.6; H, 14.4; MR_D 23.1. Found: C, 85.3; H, 14.4; MR_D 23.9.

A mixture of 40 cc. (0.4 mole) of methylcyclobutane, 108 cc. (1.2 moles) of benzene, and 50 cc. of 96% sulfuric acid was stirred for two and one-half hours at $2-4^\circ$. The hydrocarbon layer was separated and washed with cold 96% sulfuric acid, followed by water, dilute caustic, and water. The hydrocarbon mixture was first separated into methylcyclobutane-benzene and higher boiling residue. Methylcyclobutane was then fractionated from the former (20 cc. recovered; b. p. $35.2-35.8$ at 751 mm.; n_D^{20} 1.3870; d_4^{20} 0.693). The higher boiling material (5 cc.) was separated into two main fractions which boiled at $197-212^\circ$ (1.5 cc.), and $245-255^\circ$ (0.8 cc.), respectively.

The main constituent of the $197-212^\circ$ fraction was identified as *t*-amylbenzene.⁴ Its diacetamino derivative melted at $180-181^\circ$, and its melting point was not depressed by admixture of the diacetamino derivative of *t*-amylbenzene. There was also a small amount of di-*n*-amylbenzene which was isolated in the form of its diacetamino derivative which melted above 260° .

Anal. Calcd. for $C_{20}H_{32}N_2O_2$: N, 8.43. Found: N, 8.80.

The fraction boiling at $245-255^\circ$ was presumably a mixture of mono- and di-*n*-amylbenzenes.

Anal. Calcd. for $C_{11}H_{16}$: C, 89.1; H, 10.9. Calcd. for $C_{14}H_{20}$: C, 88.0; H, 12.0. Found: C, 88.8; H, 10.9.

Cyclopentane, Benzene and Sulfuric Acid.—Fifty cc. (0.54 mole) of cyclopentane was added during one hour to a cold ($2-4^\circ$), stirred mixture of 100 cc. (1.1 moles) of benzene, and 50 cc. 96% sulfuric acid. Distillation of the hydrocarbon layer showed it to be a mixture of cyclopentane and benzene. The catalyst acid did not contain ester.

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Summary

Cyclopropane and methylcyclobutane alkylate benzene in the presence of cold 96% sulfuric acid to give *n*-propyl and *t*-amylbenzene, respectively. Cyclopentane does not alkylate benzene under the same experimental conditions.

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