recrystallized from alcohol. It melted at 204°, and showed no depression in melting point when mixed with *epi*-stigmastanol prepared by the hydrogenation of stigmastanone.

Anal. Calcd. for $C_{22}H_{52}O$: C, 83.4; H, 12.4. Found: C, 83.4; H, 12.6.

It formed an acetate, m. p. 84°, which showed no depression in melting point when mixed with authentic *epi*-stigmastyl acetate.

***epi*-Stigmasterol.**—A Grignard reagent was prepared by adding a solution of 22 g. of carefully purified stigmasteryl chloride[6] in 200 cc. of dry ether over a period of four hours to a well-stirred mixture of 2 g. of magnesium, 10 drops of ethyl bromide and 10 cc. of ether. The mixture was stirred and refluxed for twenty hours. The resulting Grignard solution was oxidized, and treated as described for the preparation of *epi*-sitosterol. Seven grams of a mixture of stigmasterol and *epi*-stigmasterol was isolated. Five grams of this mixture was treated with digitonin in the same manner as described for the previous preparation. In this manner the filtrate from the digitonide, which weighed 10 g., yielded a first crop which was apparently an unsaturated hydrocarbon. The mother liquors were concentrated to give a crude product, m. p. 122–140°. After seven crystallizations from alcohol, *epi*-stigmasterol, m. p. 151°, was obtained.

Anal. Calcd. for $C_{29}H_{48}O$: C, 84.4; H, 11.7. Found: C, 84.4; H, 11.8.

Fifty milligrams of this sterol was acetylated as described for the preparation of *epi*-sitosteryl acetate. The product, after crystallization from methanol, melted at 98°.

Anal. Calcd. for $C_{31}H_{50}O_2$: C, 81.9; H, 11.1. Found: C, 82.3; H, 11.2.

Catalytic Hydrogenation of *epi*-Stigmasterol.—A solution of 200 mg. of *epi*-stigmasterol in 150 cc. of ether and 20 cc. of acetic acid was shaken for one hour with 0.4 g. of platinum oxide catalyst in a hydrogen atmosphere at 45 lb. (3 atm.) pressure. The catalyst was filtered, the ether evaporated and the residual acetic acid solution cooled. The crude *epi*-stigmastanol was filtered and crystallized from alcohol. The purified product, melting at 203°, showed no depression in melting point when mixed with *epi*-stigmastanol prepared by the reduction of stigmastanone in acid solution.

Anal. Calcd. for $C_{29}H_{52}O$: C, 83.4; H, 12.4. Found: C, 83.4; H, 12.6.

It formed an acetate, m. p. 83°, which did not depress the melting point of authentic *epi*-stigmastyl acetate.

Anal. Calcd. for $C_{31}H_{54}O_2$: C, 81.2; H, 11.8. Found: C, 81.0; H, 11.8.

Summary

epi-Sitosterol and *epi*-stigmasterol have been prepared by oxidation of the Grignard reagents from the corresponding chlorides. Both *epi*-sitosterol and *epi*-stigmasterol are very readily dehydrated. Upon hydrogenation, they yield *epi*-stigmasterol.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE UNIVERSAL OIL PRODUCTS COMPANY AT ARMOUR INSTITUTE OF TECHNOLOGY]

Alkylation with a Hydrogenating Catalyst

BY V. I. KOMAREWSKY

Recently[1] it was found that aromatic and naphthene hydrocarbons can undergo a destructive alkylation under the action of a specially prepared nickel–alumina catalyst.[2] In this article a direct alkylation of aromatic (benzene) and naphthene (cyclohexane) hydrocarbons with an olefin (ethylene) in the presence of the same catalyst will be described.

Ethylene and benzene passed over nickel–alumina catalyst at 350° produced a liquid boiling at 79–110°. This product was completely free from unsaturated hydrocarbons (stable toward permanganate). By fractionation it was possible to isolate and identify toluene (5% of the benzene charged). The bottoms after distillation contained crystals (2% of the benzene charged) which were identified as a mixture of naphthalene and diphenyl. The gas produced by the reaction contained hydrogen, methane and ethane.

Benzene alone under the same conditions remained practically unchanged. Diphenyl crystals were found in the bottoms after distillation of the liquid product; traces of hydrogen were found in the gas. These results show that a direct alkylation of benzene with ethylene takes place, but according to the previous observation[1] the ethylbenzene formed decomposes in contact with nickel–alumina to toluene and methane. Hydrogen was produced along with the formation of naphthalene.

Ethylene and cyclohexane passed over the same catalyst at 300° produced a liquid boiling at 78–100°, free from unsaturated hydrocarbons (permanganate test). By fractionation of this liquid,

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(1) Ipatieff and Komarewsky, THIS JOURNAL, **58**, 922 (1936).

(2) Zelinsky and Komarewsky, *Ber.*, **57**, 667 (1924).

toluene amounting to 5% of the cyclohexane charged was isolated. The reaction gases contained hydrogen, methane and ethane. These results show that the following reactions take place when cyclohexane and ethylene are passed over nickel–alumina catalyst.

1. Cyclohexane dehydrogenates to benzene.
2. Benzene is alkylated with ethylene to form ethylbenzene.
3. Ethylbenzene decomposes to toluene and methane.

No alkylation of naphthenic hydrocarbon takes place, but cyclohexane is first dehydrogenated to benzene and this is then alkylated with the ethylene present.

Cyclohexane alone under these conditions produces pure benzene and hydrogen.[3] Ethylene alone passed over the nickel–alumina catalyst at 300–350° gives no liquid but decomposes to carbon, hydrogen, methane and ethane (no olefins). This is in accordance with the results of other investigators,[4] showing that even our nickel–alumina catalyst is not mild enough for ethylene and decomposes the largest part of it in the alkylation experiments described above.[5]

Experimental Part

Apparatus and Procedure.—The liquid hydrocarbon was passed at a rate of 8 to 10 cc. per hour through a glass tube filled with 40 g. of catalyst. Ethylene was passed at a rate of 1.5 to 2.0 liters per hour. The tube was heated in a constant temperature electric furnace. The liquid product of the reaction was fractionated through a micro-Podbielniak column. The gases were analyzed by the Goeckel method.

Materials.—Benzene ($n^{25}\mathrm{D}$ 1.4985) and cyclohexane ($n^{25}\mathrm{D}$ 1.4260) were C. P. Eastman products.[6] Ethylene (Ohio Co.). The nickel–alumina catalyst was prepared according to the Zelinsky–Komarewsky procedure.

Alkylation of Benzene.—One hundred grams of benzene and 20.4 liters of ethylene at 350° yielded 105.5 g. of a liquid completely stable to permanganate, $n^{25}\mathrm{D}$ 1.4950. The liquid was separated into two fractions: fraction A, b. p. 79–82°, 77 g.; fraction B, b. p. 82–up, 17 g. Fraction B was refractionated giving 5.0 g. of a product, b. p. 105–110°, $n^{30}\mathrm{D}$ 1.4930. The nitration of this product yielded 2,4-dinitrotoluene, m. p. 70°. Oxidation with permanganate yielded benzoic acid, m. p. 120°.

Anal. Calcd. for $C_6H_5CH_3$: C, 91.3; H, 8.7. Found: C, 91.0; H, 8.85; mol. wt., 88.

The bottoms, 2 g., after fractionation of the liquid, solidified and gave, after recrystallization from benzene, white crystals melting around 80°. These crystals had a characteristic odor of naphthalene and gave a positive naphthalene reaction with aluminum chloride–chloroform (green color). The gas from the reaction had the following composition: H, 30.5%; paraffins, 69.5% (index 1.3).

Alkylation of Cyclohexane.—One hundred grams of cyclohexane and 15 liters of ethylene yielded at 300° 91 g. of a liquid completely stable toward permanganate, $n^{30}\mathrm{D}$ 1.4528. The product was fractionated into two fractions: fraction A, b. p. 78–80°, 75.0 g., $n^{30}\mathrm{D}$ 1.4520; fraction B, b. p. 105–110°, 5.2 g., $n^{30}\mathrm{D}$ 1.4910. Fraction B was completely soluble in fuming sulfuric acid and on nitration gave 2,4-dinitrotoluene, m. p. 70°.

Anal. Calcd. for $C_6H_5CH_3$: C, 91.3; H, 8.7. Found: C, 91.1; H, 8.6. The reaction gas contained: H, 50.8%; paraffins, 49.2% (index 1.4).

The author wishes to acknowledge the assistance of Mr. Gordon Snider in the experimental work.

Summary

1. An alkylation of benzene and cyclohexane with ethylene was observed in the presence of nickel–aluminum oxide catalyst.

2. Benzene and ethylene formed ethylbenzene, which decomposed to toluene and methane.

3. Cyclohexane and ethylene yielded toluene, due to the dehydrogenation of cyclohexane and alkylation of the benzene formed according to 2.

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(3) Zelinsky and Komarewsky, *Ber.*, **57**, 667 (1924).

(4) Sabatier and Senderens, *Compt. rend.*, **124**, 616, 1358 (1897); Cantelo, *J. Phys. Chem.*, **31**, 124, 246 (1927).

(5) In both alkylation experiments, carbon deposition on the catalyst was noticed.

(6) Cyclohexane was treated with fuming sulfuric acid, 15 per cent. sulfur trioxide, washed, dried, and distilled over metallic sodium.