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Radical Skeletal Rearrangement of Butylbenzenes over Chromia-Alumina Catalyst¹

Sir:

The catalytic skeletal isomerization of butylbenzenes via a cationic mechanism is well established in the literature.²⁻⁴ We wish now to report skeletal rearrangement of butylbenzenes catalyzed by a nonacidic chromia-alumina-B which is of a radical type. This will become evident from the reactions of *t*-butylbenzene and from 2-phenyl-2-¹⁴C-butane.

The catalyst was prepared from an alumina, obtained from potassium aluminate,⁵ which was impregnated with chromic acid according to the method described previously.⁶ It was shown that this catalyst does not contain acidic sites which can cause skeletal isomerization of hydrocarbons via a cationic mechanism.⁶

***t*-Butylbenzene.** This hydrocarbon underwent rearrangement when passed over chromia-alumina-B at 481° and an hourly liquid space velocity of 0.77. The extent of reaction was 11.3% and the product consisted of 30.5% isobutylbenzene (1), 49.4% β,β-dimethylstyrene (2), and 20.1% isobutenylbenzene (3). The reaction was highly selective, as less than 0.1% of secondary products was obtained. The fact that benzene and isobutylene were not produced is an indication that the chromia-alumina-B did not contain catalytic acidic sites.

The course of the reaction can be explained as shown in Scheme I. The chromium-carbon bond ruptures, under the influence of temperature, to generate a radical which can then rearrange. Radical rearrangement of *t*-butylbenzene in solution was reported by one of us previously.⁷ The mechanism of the removal of a hydrogen atom in an alkane system was proposed by Burwell and co-workers.⁸ No rearrangement of *t*-butylbenzene was detected over alumina as such under similar conditions.

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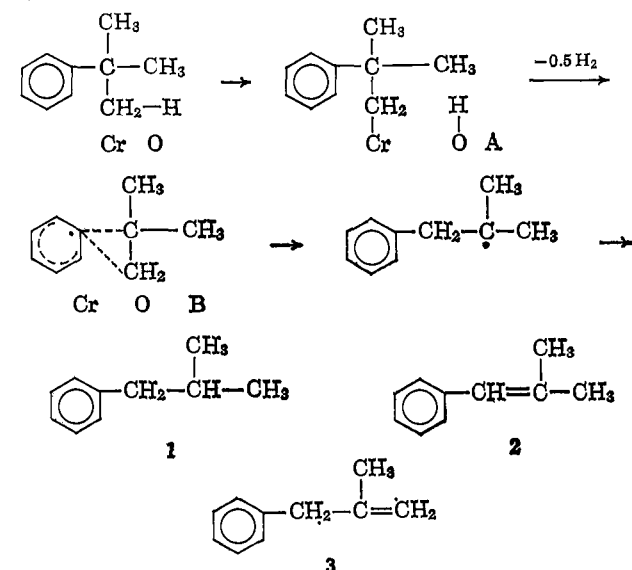
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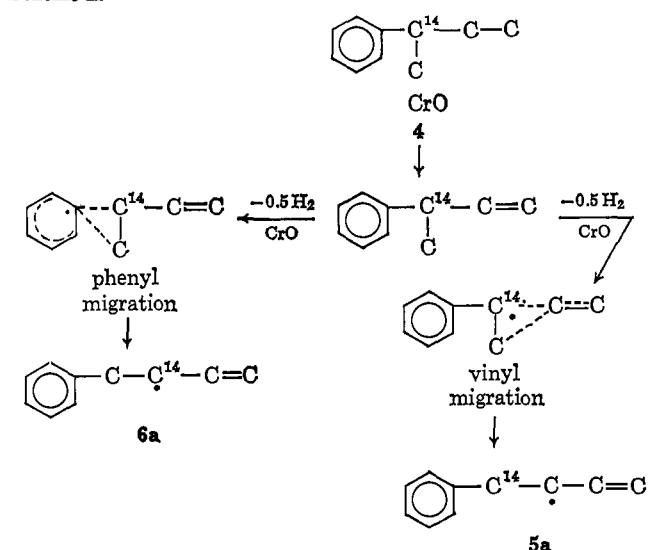
Scheme I



2-Phenyl-2-¹⁴C-butane (4). At 487° about 15% of this hydrocarbon underwent reaction of which 35% rearranged to aromatics, which after selective hydrogenation consisted of *n*-butylbenzenes composed of about equal amounts of C₆H₅¹⁴CH₂CH₂CH₂CH₃ (5) and C₆H₅CH₂¹⁴CH₂CH₂CH₃ (6). This novel rearrangement to compound 5 can be explained by a radical mechanism involving methyl-carbon insertion (vinyl migration), while the formation of compound 6 can be explained by a phenyl migration. The distribution of the ¹⁴C in *n*-butylbenzene was determined by measuring the total radioactivity of the molecule and the radioactivity of benzoic acid, obtained from the oxidation of the butylbenzene with potassium permanganate.

The course of the reaction is presented in Scheme II.

Scheme II



The methyl-carbon insertion (vinyl migration) via a radical mechanism has been recently reported by Raley and co-workers using iodine.⁹

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