[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MOUNT ALLISON UNIVERSITY]

Tertiarybutylbenzenes. IV. Mechanism of Friedel-Crafts Cyclialkylations with *tert*-Butyl Chloride. Comparative Alkylations with 2-Chloro-2,5-dimethylhexane

L. ROSS C. BARCLAY AND JOHN W. HILCHIE

Received December 26, 1956

Friedel-Crafts alkylations of *p*-di-*tert*-butylbenzene and of benzene with 2-chloro-2,5-dimethylhexane produced 1,1,4,4,5,5,8,8-octamethyl-1,2,3,4,5,6,7,8-octahydroanthracene (I). The significance of this finding relative to the mechanism of formation of (I) from alkylations using *tert*-butyl chloride is discussed.

An earlier communication[1] reported the formation of 1,1,4,4,5,5,8,8-octamethyl-1,2,3,4,5,6,7,8-octahydroanthracene (I) from the alkylation of 1,3,5-tri-*tert*-butylbenzene or *p*-di-*tert*-butylbenzene with *tert*-butyl chloride. A mechanism for this unusual cyclialkylation was proposed which involved the formation of isobutane and a tri-*tert*-butylbenzenecarbonium ion (II). It was suggested that a six-membered ring formed from the latter by addition and cyclialkylation involving isobutylene.

There are two inherent objections to this proposed mechanism. In the first place it involves a high energy primary carbonium ion, and secondly this neophyl cation (II) would be expected to rearrange readily to the more stable tertiary carbonium ion (III) before taking up isobutylene. Then subsequent cyclialkylation of (III) with isobutylene would lead to isomers of octamethyloctahydroanthracene other than (I). Lien and MacCaulay[2] have postulated the rearrangement of a carbonium ion such as (II) to account for the formation of β-alkylstyrenes when *tert*-butylbenzene is treated with hydrogen fluoride and boron trifluoride. This result is illustrated by the equations B.

In view of these objections, a more plausible explanation for these cyclialkylations can be derived from the recent results of Condon[3] who discovered that on contact with aluminum chloride *tert*-butyl chloride produces a small yield of 2,5-dichloro-2,5-dimethylhexane. This result is summarized by the equations C.

The 2,5-dimethyl-2-hexyl carbonium ion (IV) provides the required carbon skeleton for the production of (I). The present experiments prove the ability of the ion (IV) to replace the *tert*-butyl groups on the aromatic nucleus and then cyclize to form the required six-membered ring. *p*-Di-*tert*-butylbenzene is thus converted in good yield into (I) most probably by the scheme shown by the equations D. This scheme also accounts for the formation of isobutane which was detected in earlier experiments.[1]

This mechanism requires a rather congested transition state with two tertiary alkyls *ortho* to each other on the aromatic nucleus. Proton migrations to *ortho* positions are also implied. A reasonable alternative would be to suppose that a 2,5-dimethyl-2-hexyl cation will directly displace a *tert*-butyl cation, thus producing *p*-(2,5-dimethyl-2-hexyl)-*tert*-butylbenzene as the first intermediate. Our experiments cannot distinguish between these two alternatives. It would appear to be necessary to use both schemes to account for the formation of (I) from 1,3,5-tri-*tert*-butylbenzene.

Benzene could not be cyclialkylated with 2-chloro-2,5-dimethylhexane under similar conditions to those which produced (I) with 2,5-dichloro-2,5-dimethylhexane.[1] However, when two moles of aluminum chloride per mole of benzene were used under the special conditions of these experiments, a 10% yield of (I) was obtained.

In this case the cyclization of (V) requires a carbonium ion at position 5 of the 2,5-dimethyl-2-hexyl side chain. To accomplish this, it is conceivable that a hydride ion could be transferred to a proton and be expelled as hydrogen or it could undergo exchange with the chlorine of another molecule of 2-chloro-2,5-dimethylhexane. The latter seems more reasonable and accounts for the low yield of (I).

Before Bartlett's[4] identification of 1,3,5-tri-*tert*-butylbenzene (m.p. 72.5–73.0°), a compound of m.p. 128° had been reported at various times in the literature as tri-*tert*-butylbenzene[5] and as 1,2,4-tri-*tert*-butylbenzene.[6] This compound has also been reexamined by Bartlett. The structure suggested above seems most unlikely since Brown[7] has shown that it is highly improbable that two *tert*-butyl groups can occupy adjacent positions in the benzene ring. In the light of the present work, it would

---

(1) L. R. C. Barclay and E. E. Betts, *J. Am. Chem. Soc.*, **77**, 5736 (1955).

(2) A. P. Lein and D. A. MacCaulay, *J. Am. Chem. Soc.*, **75**, 2411 (1953).

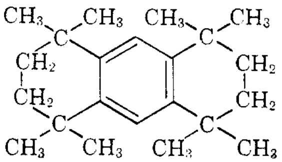
(3) F. E. Condon, *J. Org. Chem.*, **21**, 761 (1956).

(4) P. D. Bartlett, M. Roha, and R. M. Stiles, *J. Am. Chem. Soc.*, **76**, 2349 (1954).

(5) M. Senkowski, *Ber.*, **23**, 2412 (1890).

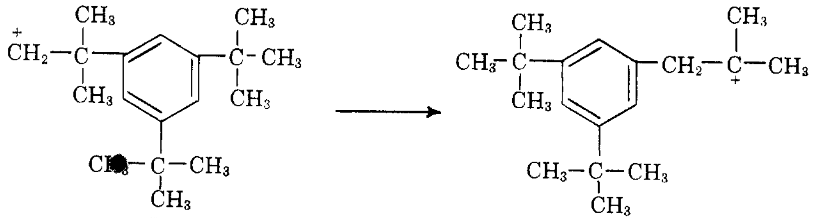
(6) R. A. Smith, *J. Am. Chem. Soc.*, **55**, 3718 (1933).

(7) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 24 (1953).



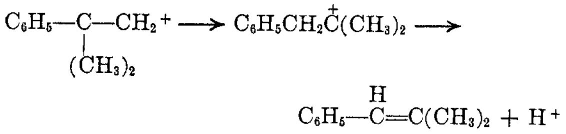
I

A



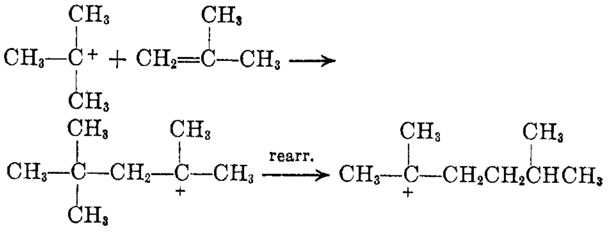
II III

B



$$C_6H_5-\underset{(CH_3)_2}{C}-CH_2^+ \longrightarrow C_6H_5CH_2\overset{+}{C}(CH_3)_2 \longrightarrow C_6H_5-\overset{H}{C}=C(CH_3)_2 + H^+$$

C

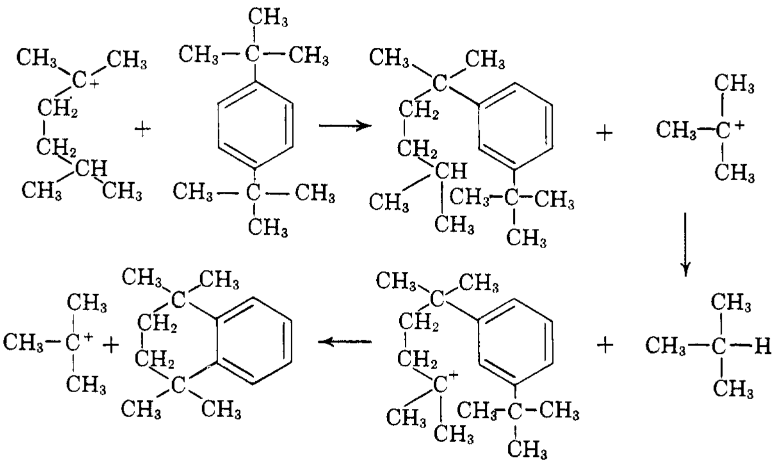


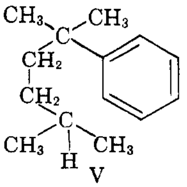
$$CH_3-\underset{CH_3}{\overset{CH_3}{C^+}} + CH_2=\overset{CH_3}{C}-CH_3 \longrightarrow$$

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{+}{\overset{CH_3}{C}}-CH_3 \xrightarrow{\text{rearr.}} CH_3-\underset{+}{\overset{CH_3}{C}}-CH_2CH_2\overset{CH_3}{C}HCH_3$$

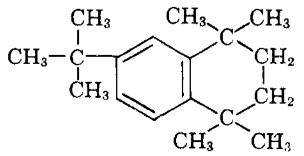
IV

D





V



VI

appear that a reasonable structure for this compound would be (VI). This compound would be practically indistinguishable from tri-*tert*-butylbenzene in the ultimate analyses. Experiments are presently being conducted to test this suggestion.

EXPERIMENTAL

Ultraviolet spectra were recorded on a Beckmann DU Spectrophotometer in cyclohexane. Melting points were done on a Fisher-Johns apparatus and are uncorrected.

2,5-Dimethyl-2-hexanol. A Grignard reagent was prepared from 127 g. (0.84 mole) of freshly distilled isoamyl bromide and 20 g. (0.84 mole) of magnesium. To this reagent was added dropwise 49 g. (0.84 mole) of acetone in an equal volume of anhydrous ether. After the initial vigorous reaction the reaction mixture was left overnight. The product was decomposed with ice and then poured into 10% sulfuric acid and the organic layer separated and dried over anhydrous sodium sulfate. After removal of the ether on the steam cone, the residue was fractionated in a Podbielniak-type column. A yield of 30 g. of the alcohol distilling at 152–155°, $n_D^{11.4}$ 1.4250 (lit.,[1] b.p. 152–154°, $n_D^{11.4}$ 1.42428) was obtained.

2-Chloro-2,5-dimethylhexane. 2,5-Dimethyl-2-hexanol (13 g., 0.10 mole) was shaken intermittently with 42 ml. of concentrated hydrochloric acid over a 1-hr. period. Fresh acid was charged into the separatory funnel and this process was repeated. The organic layer was dried over anhydrous sodium sulfate and then distilled under reduced pressure. The yield of 2-chloro-2,5-dimethylhexane, $b.p._{20\ mm.}$ 58°, n_D^{15} 1.4255; (lit.,[8] $b.p._{14\ mm.}$ 44–45°, n_D^{15} 1.42495) amounted to approximately 50%.

Alkylations. (1) p-Di-tert-butylbenzene. A solution of 2-chloro-2,5-dimethylhexane (3 g., 0.02 mole) and *p*-di-*tert*-butylbenzene (1.90 g., 0.01 mole) in 5 ml. of carbon bisulfide was cooled below 0° in an ice salt bath. Powdered anhydrous aluminum chloride (2.66 g., 0.02 mole) was added in small portions to the stirred reaction mixture over a period of 2 hr. During this time there was copious evolution of hydrogen chloride and a brown complex formed at the bottom of the reaction mixture. After a total of 4 hr. reaction time, the complex was decomposed in water and allowed to stand overnight. The semisolid organic layer was extracted with ether and the ether solution concentrated to yield colorless needles, 1.20 g., yield 40%. This product softened above 200° and melted at 220°. A sample recrystallized from ethanol-benzene proved to be identical (by mixed melting point and ultraviolet spectra) to the octahydrooctamethylanthracene (m.p. 220°) reported earlier.

(2) Benzene. A mixture of benzene (3.1 g.) and 2-chloro-2,5-dimethylhexane (3.0 g.) was treated with catalytic amounts of anhydrous aluminum chloride (0.1 g.) below 0°. No observable reaction took place in the cold. The reaction mixture was then left at room temperature for two days. However, working up of the product yielded only volatile liquids and no trace of solid hydrocarbon.

In a second experiment a mixture of 2-chloro-2,5-dimethylhexane (3.0 g., 0.02 mole) and benzene (0.78 g., 0.01 mole) was cooled below 0°. Anhydrous aluminum chloride (2.66 g., 0.02 mole) was added in small portions over a 3-hr. period to the reaction mixture kept below 0°. After about 3 hr. reaction time a few milliliters of carbon bisulfide was added to facilitate stirring of the semisolid mass. The reaction was continued for a total of 8 hr. after which time the temperature had risen to 20°. The complex was decomposed in water and after standing overnight a crystalline crust formed in the hydrocarbon layer. Extraction with ether and concentration of the ether yielded 0.31 g. of colorless needles. This product proved to be identical with octamethyloctahydroanthracene by mixed melting point and ultraviolet spectrum.

Acknowledgments. The authors express their thanks to the National Research Council of Canada for financial assistance. We are indebted to G. A. Harrington of the Indoil Chemical Company, Chicago, for a generous sample of *p*-di-*tert*-butylbenzene.

SACKVILLE, N. B.
CANADA

---

[8] *Beilstein*, I, 422.

[CONTRIBUTION FROM E. I. DU PONT DE NEMOURS & CO., INC., EASTERN LABORATORY]

Reaction of Nitric Oxide with Nitrosocyclohexane Dimer

L. G. DONARUMA AND D. J. CARMODY

Received October 29, 1956

The reaction of nitric oxide with bisnitrosocyclohexane has been studied. The possibility that an adduct of nitric oxide with the nitroso compound is formed and rearranges to cyclohexyldiazonium nitrate is discussed. A rationalization for the formation of the products, cyclohexyl nitrate, cyclohexyl nitrite, and nitrocyclohexane, by decomposition of the diazo nitrate is presented.

The reaction of nitric oxide with hydrocarbons (I) has been studied by other investigators.[1] The major products of this reaction are the nitrate (II), the nitroparaffin (III), and the nitrite (IV). We have studied the reaction of nitric oxide with cyclohexane in the presence of various dehydrogenation catalysts and obtained similar products.

$$\underset{(I)}{RH} \xrightarrow{\overset{\Delta}{NO}} \underset{(II)}{RONO_2} + \underset{(III)}{RNO_2} + \underset{(IV)}{RONO}$$

(Subscript "a" indicates that R = cyclohexyl.)

$$I_a \xrightarrow[NO]{\overset{\Delta}{Catalyst}} II_a + III_a + IV_a + C_6H_{11}OH + \text{traces of nitroolefins and carbonyl compounds}$$

Catalyst = Pt, Pd, S, NO_2

Brown[2] suggested that nitroso compounds (V) are intermediates in the reaction of nitric oxide with hydrocarbons. We allowed nitrosocyclohexane to react (V_a) with nitric oxide and obtained cyclohexyl nitrate (II_a), nitrocyclohexane (III_a), and cyclohexyl nitrite (IV_a) as the major products. Brown[2] suggested that diazo nitrates (VII) are formed by the reaction of nitric oxide with nitroso compounds (V) and that the isolable products are formed by the decomposition of the diazo nitrate followed by reaction of the decomposition products with oxides of nitrogen present in the reaction mixture.[2,3]

$$1/2(C_6H_{11}NO)_2 \rightarrow \underset{V_a}{C_6H_{11}NO} \xrightarrow[\substack{25°–50° \\ 1–6\ atm.}]{NO} II_a + III_a + IV_a + \text{traces of carbonyl compounds and other nitrated products}$$

---

[1] Burkhard, Brown, Herrick, Myers, and Hurd, paper presented at the 126th Meeting, American Chemical Society, New York, N. Y., September 1954.

[2] Brown, paper presented at the 126th Meeting, American Chemical Society, New York, N. Y., September 1954.

[3] Gray and Yoffe, *Quart. Revs.*, 362 (1955).