that $[E] = 0.0932$ mg. protein-nitrogen/ml., $[S]_0 = 21.8 \times 10^{-3}$ *M* and $\Delta t = 5.0$ minutes with the reaction as represented by equations 1 to 3 inclusive being allowed to proceed to an extent of approximately 70%. These data when evaluated *via* a $\left(\int_0^t [S]dt\right) / ([S]_0 - [S]_t)$ *vs.* $[S]_t$ plot, in which $\int_0^t [S]dt$ was approximated through the use of equation 6 without regard for the remainder term of this equation, gave a value of $k_3' = 7.86 \times 10^{-3}$ *M*/min./mg. protein nitrogen/ml., a value of $K_S' = 4.69 \times 10^{-3}$ *M* and a value of $v_0 = 2.32 \times 10^{-4}$ *M*/min. From the above values of k_3' and K_S' and the other known parameters of the system the quantity $m[S]_0^{(4)}h^5/90$ was evaluated and found to be but 6.86×10^{-6}% of the total area thus providing complete justification for ignoring the remainder term of equation 6 in the evaluation of $\int_0^t [S]dt$ in this particular instance.

It will be recognized that the plot of $\left(\int_0^t [S]dt\right) / ([S]_0 - [S]_t)$ *vs.* $[S]_t$ described in this communication has many points in common with the plot of $t/(\ln([S]_0/[S]_t))$ *vs.* $([S]_0 - [S]_t)/(\ln([S]_0/[S]_t))$ described in an earlier communication from these laboratories[8] and that both of these plots are related to the $[S]_0/v_0$ *vs.* $[S]_0$ plot of Lineweaver and Burk.[12] However it should be noted that the latter plot requires the separate evaluation of the initial velocities and even if this operation is performed in an objective manner[13] this plot can be used only for the evaluation of data obtained in the initial stages of a reaction represented by equations 1 to 3 inclusive provided that K_P is substantially greater than K_S. As this latter information is not disclosed by a $[S]_0/v_0$ *vs.* $[S]_0$ plot, or by either of its two variants,[8] it is clear that the use of these three plots is accompanied by some uncertainty in the absence of knowledge of the relative magnitudes of K_P and K_S particularly since it has been observed[14] that with certain but not all specific substrates of α-chymotrypsin K_P may be substantially less than K_S when K_P is evaluated from experiments conducted in the absence of added hydrolysis products.

In principle a $\left(\int_0^t [S]dt\right) / ([S]_0 - [S]_t)$ *vs.* $[S]_t$ plot should be equivalent to a $t/(\ln([S]_0/[S]_t))$ *vs.* $([S]_0 - [S]_t)/(\ln([S]_0/[S]_t))$ plot,[8] a $t/([S]_0 - [S]_t)$ *vs.* $(\ln([S]_0/[S]_t))/([S]_0 - [S]_t)$ plot,[8] or a $([S]_0 - [S]_t)/t$ *vs.* $(\ln([S]_0/[S]_t))/t$ plot.[6,7] Therefore, it is of interest to compare the values of k_3', K_S' and v_0 obtained from a $\left(\int_0^t [S]dt\right) / ([S]_0 - [S]_t)$ *vs.* $[S]_t$ plot with the comparable values obtained from a $([S]_0 - [S]_t)/t$ *vs.* $(\ln([S]_0/[S]_t))/t$ plot[6,7] using in each instance the same experimental data. It was noted above that the experimental data represented in Fig. 1 gave, on the basis of a $\left(\int_0^t [S]dt\right) / ([S]_0 - [S]_t)$ *vs.* $[S]_t$ plot, a value of $k_3' = 7.86 \times 10^{-3}$ *M*/min./mg. protein nitrogen/ml., a value of $K_S' = 46.9 \times 10^{-3}$ *M* and a value of $v_0 = 2.32 \times 10^{-4}$ *M*/min. When the same experimental data were evaluated through the use of a $([S]_0 - [S]_t)/t$ *vs.* $(\ln([S]_0/[S]_t))/t$ plot[6,7] it was found that $k_3' = 8.09 \times 10^{-3}$ *M*/min./mg. protein nitrogen/ml., $K_S' = 48.8 \times 10^{-3}$ *M* and $v_0 = 2.33 \times 10^{-4}$ *M*/min.

In practice it has been observed that for reactions which may be represented by equations 1 to 3 inclusive the plot based upon equation 5 is better suited for treating data that have been obtained during the initial stages of a given reaction, *i.e.*, for a lesser extent of reaction, than are the three alternative plots which are derived by indefinite integration and rearrangement of the common differential rate equation. In addition there is less numerical work involved in evaluating experimental data with the first plot than with the other three. However, as has been noted previously[8] this latter factor of convenience may be outweighed by other considerations.

As all of the plots considered above are useful only when the reaction in question has been allowed to proceed to an extent compatible with the evaluation of K_P, which will be determined not only by the magnitude of K_P but also by the relative magnitudes of K_P and K_S we are now engaged in exploring the possible use of methods involving numerical differentiation since such methods would be useful and desirable in those cases where reactions proceed only at very low velocities and where extended times of observation are not desirable.

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The *t*-Butylbenzenes. II. A High Melting Hydrocarbon from Friedel–Crafts Alkylation of 1,3,5-tri-*t*-butylbenzene with *t*-Butyl Chloride[1]

BY L. ROSS C. BARCLAY AND EILEEN E. BETTS[2]

RECEIVED APRIL 25, 1955

In part 1[3] we reported a compound, $C_{22}H_{34}$, m.p. 218.5–219°, obtained by Friedel–Crafts alkylation of 1,4-di-*t*-butylbenzene with *t*-butyl chloride below 0°. The empirical formula $C_{22}H_{34}$, the ultraviolet absorption spectrum, and the high melting point indicated the presence of at least one alicyclic ring in this aromatic hydrocarbon. In this communication experimental evidence is presented which elucidates the structure of this compound.

Bartlett and co-workers[4] alkylated 1,4-di-*t*-butylbenzene with *t*-butyl chloride to form 1,3-di-*t*-butylbenzene, 1,3,5-tri-*t*-butylbenzene and a compound, m.p. 209–210°, which is probably the same as our high melting hydrocarbon.

1,1,4,4,5,5,8,8-Octamethyl-1,2,3,4,5,6,7,8-octahydroanthracene.—The high melting hydrocarbon was dehydrogenated with palladium at about 400° in a sealed tube and the ultraviolet spectrum of the product clearly showed the presence of anthracene or an anthracene derivative. Among the possible

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(12) H. Lineweaver and D. Burk, THIS JOURNAL, **56**, 658 (1934).

(13) R. R. Jennings and C. Niemann, *ibid.*, **75**, 4687 (1953).

(14) Unpublished observations of W. Lands and R. Lutwack.

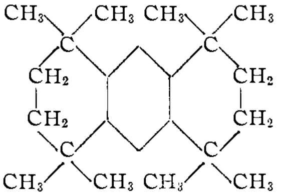
(1) Taken in part from the M.Sc. thesis of Eileen E. Betts.

(2) Recipient of a National Research Council of Canada Bursary.

(3) L. R. C. Barclay and E. E. Betts, *Can. J. Chem.*, **33**, 672 (1955).

(4) P. D. Bartlett, M. Roha and R. M. Stiles, THIS JOURNAL, **76** 2349 (1954).

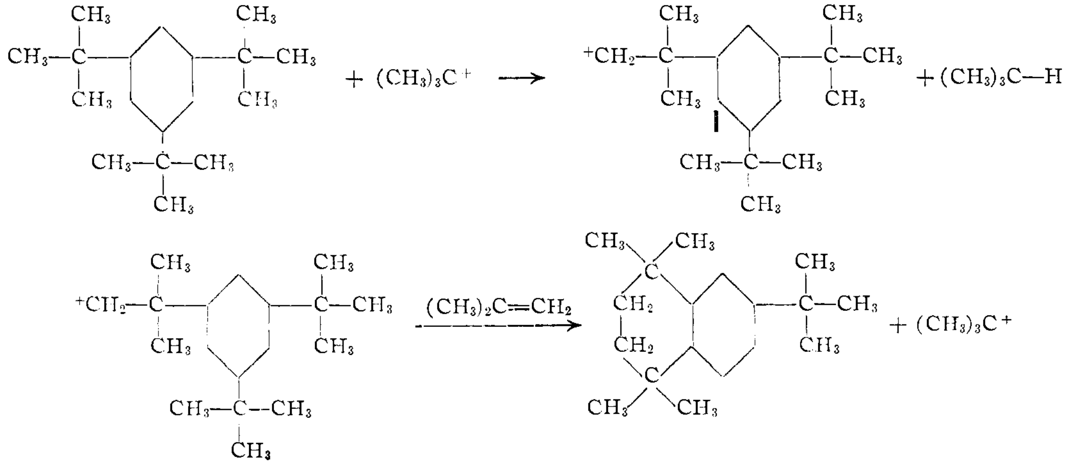
isomers with the formula $C_{22}H_{34}$ which would dehydrogenate to anthracene is octamethyloctahydroanthracene (I).



I

The high melting hydrocarbon from the alkylation of 1,4-di-*t*-butylbenzene was shown to be identical by mixed melting points and ultraviolet spectra with compound I which was prepared by the method of Bruson and Kroeger.[5]

The Mechanism of the Reaction.—The previous publication[3] suggested that 1,3,5-tri-*t*-butylbenzene was an intermediate in the formation of I from 1,4-di-*t*-butylbenzene. Alkylations reported herein (see run 4) where 1,3,5-tri-*t*-butylbenzene is converted to I support this view. The action of $AlCl_3$ on 1,3,5-tri-*t*-butylbenzene in the cold (run 1) or the action of isobutylene and $AlCl_3$ (with or without the presence of HCl) (run 2) failed to produce this reaction. Isobutylene must polymerize under these conditions before it can form *t*-butyl chloride or react with 1,3,5-tri-*t*-butylbenzene. When *t*-butyl chloride was added after passing isobutylene through the reaction I formed smoothly. Moreover on the synthesis of this compound from 1,3,5-tri-*t*-butylbenzene considerable gas was evolved besides hydrogen chloride or isobutylene. This gas was condensed in Dry Ice and the presence of isobutane shown by infrared analysis. We suggest the following scheme of reactions to explain these results.



The 1,3,5-tri-*t*-butylbenzene is so hindered as to prevent further aromatic substitution. The *t*-butylcarbonium ion initiates this reaction by extracting a hydride ion from one of the butyl groups to account for the isobutane. Once the reactive tri-*t*-butylbenzenecarbonium ion is formed it reacts with isobutylene, which is produced by elimination of hydrogen chloride from *t*-butyl chloride, before the isobutylene polymerizes. Cyclization then occurs accompanied by elimination of an *ortho* situated *t*-butyl group which is replaced by a proton. The remaining *t*-butyl group would presumably be acted upon in a similar manner to account for the second six-membered ring.

Experimental[6]

Catalytic Dehydrogenation.—Attempted dehydrogenations of the hydrocarbon $C_{22}H_{34}$ in an open tube using the catalysts platinum–charcoal, palladium–asbestos, sulfur or selenium at temperatures up to 400° were not successful due to the fact that the hydrocarbon is very volatile, beginning to sublime rapidly above 100°. Dehydrogenations were then attempted in sealed tubes. The hydrocarbon (0.1 g.) and palladium–asbestos (about 0.5 g.) were placed in a micro thick-walled carius tube which was subsequently sealed just above the contents of the tube. The sealed carius tube was placed in a furnace and heated at about 420° for 18 hours. After cooling, the tube was opened and its contents extracted with cyclohexane. The cyclohexane solution was strongly fluorescent in ultraviolet light and an ultraviolet spectrum indicated the presence of an anthracene derivative.

1,1,4,4,5,5,8,8-Octamethyl-1,2,3,4,5,6,7,8-octahydroanthracene. A. Preparation of Reagents. (i) 2,5-Dimethyl-1,5-hexadiene.—This compound was prepared by the Grignard reaction from methallyl chloride and magnesium. A solution of 46 g. of methallyl chloride (practical, dried over Na_2SO_4, distilled 71–72°) in 100 cc. of absolute ether was added slowly to 6.1 g. of magnesium turnings with cooling when the reaction became too vigorous. The reaction mixture was refluxed for one hour, some of the ether removed by fractional distillation, and water added. The organic layer was separated, dried with calcium chloride and fractionally distilled. The yield of 2,5-dimethyl-1,5-hexadiene boiling at 118–120° amounted to 9 g.

(ii) **2,5-Dichloro-2,5-dimethylhexane.**—Nine grams of 2,5-dimethyl-1,5-hexadiene was diluted with an equal volume of ethanol and dry hydrogen chloride was passed into the solution until it was saturated. Heating accompanied the reaction. After cooling, white crystals separated from the reaction mixture. These were separated by filtration, washed with water, then with methanol and dried in a vacuum desiccator; yield 4 g. The 2,5-dichloro-2,5-dimethylhexane melted at 64° (lit.[5] m.p. 63–64°) and had a strong menthol-like odor.

B. Alkylation of Benzene.—2,5-Dichloro-2,5-dimethylhexane (3.8 g.), benzene (8.5 g., dried over sodium) and anhydrous aluminum chloride (0.11 g.) were placed in a flask fitted with a reflux condenser and drying tube. The

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[5] H. A. Bruson and J. W. Kroeger, This Journal, **62**, 36 (1940).

[6] All melting points are uncorrected. Ultraviolet absorption spectra were measured in cyclohexane with a Beckmann DU Spectrophotometer. The infrared spectrum and interpretation was carried out by the Anderson Physical Laboratory, Champaign, Illinois.

reaction proceeded smoothly for one hour with evolution of hydrogen chloride. The reaction mixture was hydrolyzed by the addition with stirring of dilute hydrochloric acid. On removal of excess benzene from the organic layer 2.5 g. of crystalline material was collected. On recrystallization from 1:1 benzene–ethanol, the 1,1,4,4,5,5,8,8-octamethyl-1,2,3,4,5,6,7,8-octahydroanthracene separated in colorless needles which melted at 220–221°. A mixture of this octamethyloctahydroanthracene with the hydrocarbon $C_{22}H_{34}$ (m.p. 218.5–219°) melted at 220°.

The nitro derivative of the substituted anthracene was prepared by dissolving 1.7 g. in a solution of 83 cc. of acetic acid and 50 cc. of acetic anhydride at 85–95° and adding 2.5 cc. of fuming nitric acid slowly with stirring. After three hours heating at 85–95° the reaction mixture was cooled and the yellow crystals which separated were collected, washed with water, then alcohol; yield 1.1 g. After recrystallization from 1:1 benzene–ethanol, the nitro derivative of octamethyloctahydroanthracene melted at 263–265°. A mixture with the nitro derivative (m.p. 267°) of the high melting hydrocarbon melted at 263–264°.

Friedel–Crafts Alkylation of 1,3,5-Tri-*t*-butylbenzene. Run 1. The Action of Aluminum Chloride.—Ten grams of 1,3,5-tri-*t*-butylbenzene was dissolved in 50 cc. of carbon disulfide and cooled to −7°. Eight grams of aluminum chloride was added over a 0.5-hour period and the reaction mixture stirred below 0° for four hours when a small aliquot was taken and decomposed in water. After evaporation of the carbon disulfide an ultraviolet spectrum of the white crystals, m.p. 70°, was determined. It did not differ from the spectrum of pure 1,3,5-tri-*t*-butylbenzene.

Run 2. The Action of Isobutylene with Hydrogen Chloride.—Dry hydrogen chloride was added to the reaction mixture of run 1 at below 0° for two hours. Isobutylene was generated by dropping 85% phosphoric acid on warm *t*-butyl alcohol and passing the gas produced through an ice-trap, 85% phosphoric acid and a calcium chloride drying tube. For five hours, the isobutylene was passed into the reaction mixture which absorbed it rapidly. An aliquot of the reaction mixture was taken and decomposed in water. A spectrum of the viscous liquid remaining after evaporation of the carbon disulfide had the same absorption as 1,3,5-tri-*t*-butylbenzene and none of the characteristic peaks of octamethyloctahydroanthracene were present.

Run 3. The Addition of *t*-Butyl Chloride to the Reaction Mixture of Run 2.—*t*-Butyl chloride was added to the reaction mixture of run 2 below 0°. A gas which was not absorbed by 20% NaOH or concentrated sulfuric acid was evolved from the reaction mixture. After about an hour when 25 cc. of *t*-butyl chloride had been added, a small aliquot of the reaction mixture was taken and decomposed in water. The white solid left after the evaporation of the CS_2 melted at 210°.

Run 4. Preparation of Hydrocarbon $C_{22}H_{34}$ from 1,3,5-Tri-*t*-butylbenzene and Isolation of Isobutane.—Ten grams (0.04 mole) of 1,3,5-butylbenzene and 50 cc. of carbon disulfide were put in a flask so arranged that gases evolved during the reaction would pass through wash towers containing 20% sodium hydroxide and concentrated sulfuric acid, into a trap cooled in Dry Ice. The carbon disulfide solution was cooled to −5° and 8 g. (0.06 mole) of aluminum chloride added. Eleven grams (0.12 mole) of *t*-butyl chloride was added over a period of one hour, after which a gas was evolved continually which was not absorbed in the wash towers, but which condensed in Dry Ice. After four hours, the reaction mixture was decomposed by pouring into water, the organic layer extracted with ether, most of the ether and CS_2 evaporated and the solid which crystallized out was recrystallized from benzene–ethanol. The melting point of the colorless needles was 212–216°. A mixed melting point with the hydrocarbon (octamethyloctahydroanthracene) showed no depression. An infrared spectrum on the gas condensed in Dry Ice showed isobutane to be the only organic gas present.

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Synthesis of Disaccharides with Pea Preparations

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Leloir and Cardini[1,2] showed that enzyme preparations from wheat, corn, peas and bean germs catalyze the reversible formation of sucrose from UDPG and free fructose

$$\text{UDPG} + \text{D-fructose} \rightleftharpoons \text{UDP} + \text{sucrose} \qquad (1)$$

They also demonstrated[3] that some pea preparations contain an enzyme which will form sucrose phosphate when fructose 6-phosphate is substituted for D-fructose

$$\text{UDPG} + \text{D-fructose 6-phosphate} \rightleftharpoons \text{UDP} + \text{sucrose phosphate} \qquad (2)$$

the enzymes causing reactions (1) and (2) could not be completely separated, but sufficient evidence was presented to conclude that two enzymes are involved.

In the present communication, using preparations from green peas, we confirmed the synthesis of sucrose from UDPG and D-fructose, and of sucrose phosphate from UDPG and D-fructose 6-phosphate. We have also shown that these preparations produce three other disaccharides, D-glucosyl-D-xyluloside, D-glucosyl-D-rhamnuloside[4] and D-glucosyl-L-sorboside, according to the reactions

$$\text{UDPG} + \text{D-xylulose} \rightleftharpoons \text{UDP} + \text{D-glucosyl-D-xyluloside} \qquad (3)$$

$$\text{UDPG} + \text{D-rhamnulose} \rightleftharpoons \text{D-glucosyl-D-rhamnuloside} \qquad (4)$$

$$\text{UDPG} + \text{L-sorbose} \rightleftharpoons \text{D-glucosyl-L-sorboside} \qquad (5)$$

The disaccharide in reaction (3) is probably identical with the one formed by the action of an enzyme present in *Pseudomonas saccharophila* from D-glucose 1-phosphate and D-xylulose.[5]

Experimental

Synthesis of Sucrose and Sucrose Phosphates.—Five hundred grams of fresh peas was placed in 150 ml. of water, homogenized in a Waring blendor, the homogenate was centrifuged and the supernatant solution was fractionated with ammonium sulfate. The precipitate occurring between 20 and 50% ammonium sulfate saturation was dissolved in a minimum of water, dialyzed for 2 hr. against distilled water and then overnight against 0.05 *M* phosphate buffer, *p*H 7. The solution was adjusted to *p*H 5, the resulting precipitate dissolved in water, dialyzed again against 0.05 *M* sodium Versenate (ethylenediamine tetraacetate), *p*H 7, overnight, and then against phosphate buffer at the same *p*H to remove the Versene. The final solution, which had a volume of 7 ml., contained 5 mg. N per/ml.

The complete reaction mixture contained 0.01 ml. of

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(1) L. F. Leloir and C. E. Cardini, THIS JOURNAL, **75**, 6084 (1953).

(2) L. F. Leloir and C. E. Cardini, *J. Biol. Chem.*, **214**, 149 (1955).

(3) L. F. Leloir and C. E. Cardini, *ibid.*, **214**, 157 (1955).

(4) The D-rhamnulose was obtained by Drs. N. Palleroni and M. Doudoroff through isomerization of D-rhamnose with a bacterial enzyme (mannose isomerase) preparation from *P. saccharophila*.

(5) W. Z. Hassid, M. Doudoroff, H. A. Barker and W. H. Dore, THIS JOURNAL, **68**, 1465 (1946).