echinocystate in 70 cc. of glacial acetic acid at 70° was added with stirring a solution of 17.5 cc. of 30% hydrogen peroxide in 17.5 cc. of glacial acetic acid. The resulting solution was heated at 80° for one hour, then heated to boiling and water added to turbidity. After cooling, filtering and crystallizing from methyl alcohol, the product melted at 211–214°. Two recrystallizations raised the melting point to 215–217.5°; $[\alpha]^{22}$D $-74.2°$, $[\alpha]^{22}_{546}$ $-87.6°$ in dioxane.

Anal. Calcd. for $C_{35}H_{54}O_7$: C, 71.64; H, 9.27. Found: C, 71.47; H, 9.18.

The tetranitromethane test was negative. On attempting to acetylate the compound or to form an oxime, it was recovered unchanged.

Summary

It has been shown by oxidation that both hydroxyl groups in the triterpenoid sapogenin, echinocystic acid, are secondary and that one is β to the carboxyl group since a diketone is formed with loss of carbon dioxide. If the carboxyl group is esterified before oxidation a diketo ester is obtained which on saponification loses carbon dioxide and yields a diketone different from that formed by the direct oxidation of echinocystic acid. If one oxidizes the monoacetyl derivative of echinocystic acid in which the hydroxyl group of echinocystic acid which is not β to the carboxyl group is esterified, a monoketoacetyl derivative is formed with loss of carbon dioxide. Removal of the acetyl group by acid alcoholysis followed by oxidation yields a diketone identical with that from the methyl ester but different from that derived from the free acid. Since the esterification of the carboxyl group or of the hydroxyl group which is not β to it prevents a rearrangement, it is concluded that both hydroxyl groups and the carboxyl group must be relatively near each other.

The preparation of a bromolactone and of a hydrogen peroxide oxidation product gives additional evidence for the close relationship of echinocystic acid to hederagenin and oleanolic acid.

STANFORD UNIVERSITY, CALIF.

The Jacobsen Reaction. VI.[1] Ethyltrimethylbenzenes

BY LEE IRVIN SMITH AND MATTHEW A. KIESS[2]

In previous papers of this series, several tetrasubstituted benzenes have been investigated with respect to their behavior when subjected to the conditions of the Jacobsen rearrangement. The results may be summed up briefly as follows: of the chlorotrimethylbenzenes studied, 5- and 6-chloropseudocumenes rearranged to 3-chloropseudocumene, while the last-mentioned compound, as well as chloromesitylene and 4-chlorohemimellithene, were not rearranged by sulfuric acid but merely sulfonated. When rearrangement of these chloro compounds occurred, it was entirely intramolecular and resulted merely in the migration of a chlorine atom. The two bromotrimethylbenzenes which were studied presented a somewhat different picture in that 5-bromopseudocumene rearranged to the 3-bromo compound and at the same time there was an intermolecular transfer of bromine leading to tribromopseudocumene. In the case of bromomesitylene, the rearrangement was entirely of the intermolecular type and the products were mesitylene and polybromomesitylenes. The tetramethylbenzenes showed both types of rearrangement, durene and isodurene giving prehnitene as the main product by intramolecular rearrangement, but at the same time there were formed smaller amounts of pseudocumene and hexamethylbenzene by intermolecular transfer of methyl groups. Prehnitene was not rearranged by sulfuric acid, but merely sulfonated. The accumulated results of previous studies indicated that in the monohalotetramethylbenzenes, the decreasing ease of migration was $Br > CH_3 > Cl$, while in the monohalotrimethylbenzenes, the order was $Br > Cl > CH_3$. Moreover, when any tetra substituted benzene did rearrange intramolecularly, the main product was always a tetrasubstituted benzene in which the substituents were oriented in the 1,2,3,4-positions.

Since slight changes in the nature of the sub-

(1) Polymethylbenzenes. XXIV. Paper XXIII, THIS JOURNAL, **61**, 284 (1939). Paper V on the Jacobsen Reaction, *J. Org. Chem.*, **2**, 112 (1937).
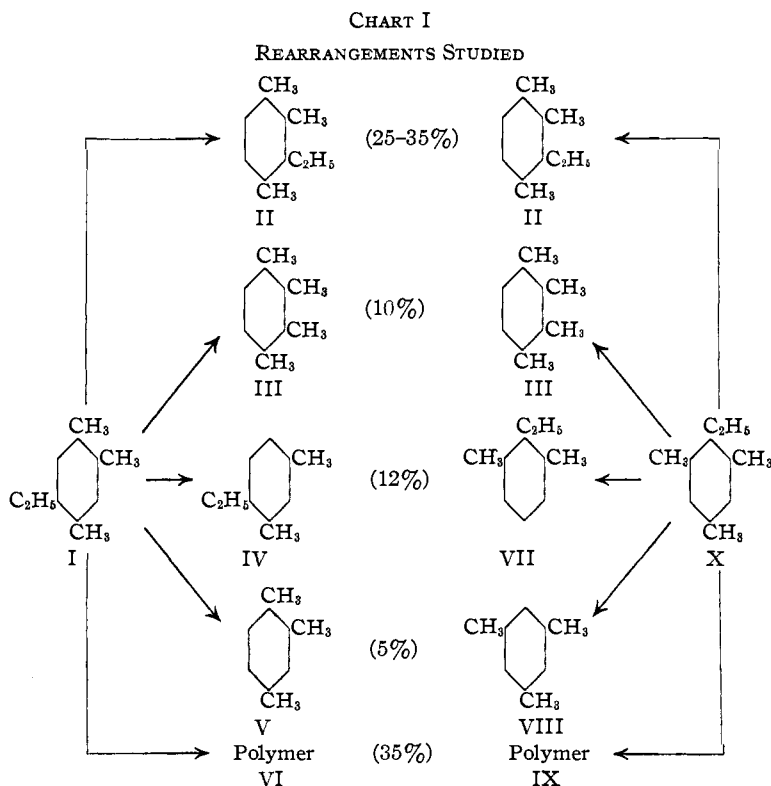
(2) Abstracted from a thesis by Matthew A. Kiess, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, November, 1938.

stituents produced differences in the ease and character of the rearrangement, certain ethyltrimethylbenzenes have now been investigated. These substances, 5-ethylpseudocumene (I), 3-ethylpseudocumene (II), and ethylmesitylene (X), have ethyl groups in place of the halogen atoms of the halotrimethylbenzenes discussed above, representatives of which undergo both types of rearrangement. Moreover, these hydrocarbons were chosen so that their structures were analogous to those of the tetramethylbenzenes durene, prehnitene, and isodurene, in which the open positions are para, ortho, and meta, respectively. Of these tetramethylbenzenes, prehnitene does not rearrange, while the other two rearrange, for the most part, *intramolecularly* into prehnitene. Finally, the ethyltrimethylbenzenes are isomeric with pentamethylbenzene, which rearranges entirely *intermolecularly* into prehnitene and hexamethylbenzene.[3]

CHART I

REARRANGEMENTS STUDIED

Of the three ethyltrimethylbenzenes, only one, 5-ethylpseudocumene (I), has previously been

(3) The terms "intramolecular" and "intermolecular," used in reference to these rearrangements in this and other papers of this series, do not presuppose a knowledge of the actual mechanisms of the reactions, but are merely terms of convenience. The terms "apparent intramolecular" and "apparent intermolecular" really should be used.

subjected to the conditions of the Jacobsen rearrangement. Töhl and Karchowski[4] reported that this hydrocarbon did not rearrange, but their conclusion was based upon the fact that the hydrocarbon obtained after treatment with sulfuric acid gave a dibromo compound which did not give a significant depression in melting point when mixed with dibromo-5-ethylpseudocumene prepared from the original hydrocarbon. This evidence is of little value as proof of structure because it has been demonstrated that perbromopolymethylbenzenes, when mixed with each other, do not give significant depressions in melting points.[5]

3-Ethylpseudocumene (II) was found to be stable as a sulfonic acid in the presence of concentrated sulfuric acid at 70° for six hours. This hydrocarbon therefore resembles the other 1,2,3,4-tetrasubstituted benzenes such as prehnitene, 3-bromo- and 3-chloropseudocumenes. Both 5-ethylpseudocumene (I) and ethylmesitylene (X) rearranged; in each case the chief product was 3-ethylpseudocumene (II) (as a sulfonic acid). In this respect these hydrocarbons resemble durene and isodurene, as well as 5- and 6-chloropseudocumenes. But the reaction was much more complicated than that of the tetramethylbenzenes or of the chloropseudocumenes, for in addition to the migration of an alkyl group, products are formed by loss of a methyl group, by loss of the ethyl group, and, most astonishing of all, by a reaction which is equivalent to loss of *part* of the ethyl group. The products are shown in the chart.

No penta- or hexasubstituted benzenes could be isolated from the reaction product, hence it is unlikely that the trisubstitution products resulted from an intermolecular rearrangement. Nor was any product found which could conceivably be formed by the introduction of the methyl group apparently lost from the ethyl group. Since IV, V, VII and VIII apparently are formed by the

(4) Töhl and Karchowski, *Ber.*, **25**, 1530 (1892).

(5) Smith and Moyle, THIS JOURNAL, **55**, 1676 (1933).

simple elimination of a methyl or ethyl group from I and X, and all the remaining groups are in place just as they are in the starting materials, it is likely that the loss of these alkyl groups occurs in the very early stages of the rearrangement. Also, since all of the products isolated are stable toward sulfuric acid, it seems most likely that the different products formed are the result of concurrent, rather than consecutive, reactions. Certainly not one of these products can be an intermediate in the formation of any of the others.

There was a vast difference observed between the ease of migration of groups in 5-ethylpseudocumene and ethylmesitylene. In this respect ethylmesitylene resembled chloromesitylene rather than isodurene; the activity of the ethyl group lay between those of a chlorine atom and a methyl group when these three compounds were compared, and the order of ease of migration for these three groups was $CH_3 > C_2H_5 > Cl$. The Jacobsen reactions were not carried out at room temperature, because ethylmesitylene sulfonic acid was stable in the presence of sulfuric acid under these conditions for over a week. Under the same conditions, 5-ethylpseudocumene sulfonic acid rearranged completely in one week. In order to obtain comparative results, both hydrocarbons were subjected to the action of sulfuric acid at 60–70°. At this temperature, one hour sufficed for the complete rearrangement of 5-ethylpseudocumene, while six hours were required for the complete change of ethylmesitylene. It is to be noted that the times required for complete rearrangement of the two hydrocarbons are inversely related to the ease with which they are sulfonated: ethylmesitylene was sulfonated at room temperature in a few minutes by shaking it with an equal volume of concentrated sulfuric acid, while 5-ethylpseudocumene remained largely unchanged in the presence of sulfuric acid for weeks. Both hydrocarbons were sulfonated quickly by shaking them with 10% oleum—five minutes sufficed for 5-ethylpseudocumene, and one or two minutes for ethylmesitylene.

There is a close parallel between the rearrangements of I and X with respect to the relative amounts of the different products that are formed, and if the main product, II in both cases, is regarded as the result of an intramolecular rearrangement, then it follows that the ethyl group migrates much more readily than does the methyl group, since I rearranges so much more rapidly

than X. The appearance of prehnitene (III) among the rearrangement products of both hydrocarbons is very difficult to explain; so also are the structures of the ethyldimethylbenzenes (IV and VII), for if these are regarded as formed by direct elimination of a methyl group, then the transformation from I to IV involves elimination of that methyl group which is meta to the ethyl group, while the transformation from X to VII requires the elimination of that methyl group para to the ethyl group. No such complications arise in the formation of V and VIII: these result simply by the elimination of the ethyl group from I and X, respectively.

The evolution of sulfur dioxide was again a characteristic feature of the rearrangement, as was the formation of the amorphous, tarry by-products (VI and IX). Efforts made to carry out the rearrangement in nitrobenzene, benzene or ligroin and so avoid the formation of the amorphous material, were uniformly unsuccessful. Whenever the amounts of these products were small, then some unchanged material was always recovered and conversely, whenever the rearrangement was carried to completion, the tarry by-product always amounted to about 30% of the weight of the starting material. The nature of these products is unknown. They are almost completely soluble in fairly large volumes of acetone or ether, giving solutions with a characteristic green fluorescence. The only definite substances which could be isolated from the tars were very small amounts (less than 5%) of nearly colorless materials, melting at 173–175° and 185–186° from 5-ethylpseudocumene and ethylmesitylene, respectively, but the amounts of these substances were too small for investigation.

Experimental Part

The preparation of the hydrocarbons and their properties are given in the previous paper.[6]

The Jacobsen Rearrangement.—A standard procedure for conducting these experiments was adopted after many preliminary experiments had shown that comparable results could be obtained if the hydrocarbons were sulfonated quickly and then the solutions of the sulfonic acids in sulfuric acid were heated to 60–70° for six hours. One example will be given. The hydrocarbon (100 g.) was sulfonated by shaking it vigorously for five minutes with 10% oleum (300 cc.). The maximum temperature reached during the sulfonation was 40°. The clear orange solution was immersed in a water-bath at 60–70° for six hours; after about thirty minutes the color had changed to brown, and sulfur dioxide began to be noticeable. After an hour,

(6) Smith and Kiess, THIS JOURNAL, **61**, 284 (1939).

Table I

Final Fractionation of the Volatile Products (62.3 G.) from the Rearrangement of 5-Ethylpseudocumene (100 G.)

Fraction	Amt., g.	B. p., °C.	p., mm.	n_D, °C.	Product	%	M. p. of nitro cpd., °C.
I	2.0	69.5-70	20	1.5015 (20)	Pseudocumene	6.7	181-183
II	2.2	70-83	21	1.5013 (21)	Pseudocumene		184
III	6.0	85	25	1.5008 (22)	4-Ethyl-m-xylene	14.4	129-131
IV	3.0	85-87.5	24	1.5020 (22)	4-Ethyl-m-xylene		131
V	2.0	91-94.5	23	1.5060 (25)	Prehnitene	11.2	173-175
VI	5.0	97-99	25	1.5070 (25)	Prehnitene		176
VII	27.0	106-108	25	1.5160 (25)	3-Ethylpseudocumene	41.7	79-80
Total recy.	47.2				Loss on fractionation	26	

Table II

Final Fractionation of the Volatile Products (60 G.) from the Rearrangement of Ethylmesitylene (100 G.)

Fraction	Amt., g.	B. p., °C.	p., mm.	$n^{22}D$	Product	%	M. p. of nitro cpd., °C.
I	4.0	60-72	25	1.5000	Mesitylene	6.7	232
II	9.5	80-83	24	1.5048	2-Ethyl-m-xylene	15.9	181
III	2.0	87-92	25	1.5107	Prehnitene		176
IV	5.0	92-100	25	1.5097	Prhenitene	16.6	176
V	3.0	100-102	25	1.5102	Prehnitene		176
VI	34.5	106-108	25	1.5122	3-Ethylpseudocumene	57.5	79-80
Total recy.	58.0				Loss on fractionation	3.3	

Table III

Fractionation of the Products from the Rearrangement of 3-Ethylpseudocumene (20 G.)

Fraction	Amt., g.	B. p., °C.	p., mm.	$n^{22}D$	Product	%	M. p. of nitro cpd., °C.
I	17	106-108	25	1.5133	3-Ethyl-pseudo-cumene	85	79-80

the color was black and the evolution of sulfur dioxide was fairly rapid. After six hours the mixture was cooled to room temperature and was carefully poured onto 80% (500 g.) of its weight of crushed ice. Usually the temperature remained at 10° or below; if not, the mixture was cooled to 10°. A semi-solid product—gray, green, or black—rose to the top and was separated mechanically; the acid layer was free from organic material. The pasty solid, when stirred with water (500 cc.), dissolved for the most part. The solution was filtered to remove a pasty white insoluble material (about 6 g.) and the sulfonic acids in the filtrate were hydrolyzed by adding about an equal volume of sulfuric acid (to bring the concentration of sulfuric acid to about 50%) and passing in steam at 140-150°. The rearranged hydrocarbons (about 60 g.) were isolated from the distillate; there remained a viscous residue (about 26 g.) in the distilling flask.

The oils were separated into their components by careful fractionation. In the first experiments, a Widmer column was used, but this proved entirely inadequate for anything even approaching a quantitative separation of the hydrocarbons present in the oils. But the Fenske column described in the previous paper[6] proved admirably adapted to handle the mixtures obtained, and the results of the fractionation of the products from one rearrangement experiment on each of the three hydrocarbons (100 g.) are given in Tables I, II, and III.

It is evident from the boiling points and indices of refraction shown in the above tables that fractionation using this column sufficed to separate each hydrocarbon quite well. By nitration each hydrocarbon was readily identified; moreover, when two hydrocarbons occurred in one fraction, a good estimate of the relative amounts of each present could be made by nitrating the mixture and fractionally crystallizing the nitro compounds.

Some difficulty was encountered in finding suitable solid derivatives which were readily prepared and which could be used for identifying the hydrocarbons resulting from the rearrangements. It has been shown previously[7] that polybromo derivatives of the tetramethylbenzenes are useless for purposes of identification since significant depressions in melting point do not result when the isomeric compounds are mixed. This same behavior was found to hold also in the case of the dibromo derivatives of ethylmesitylene and 5-ethylpseudocumene, and to extend to the sulfonanilides and sulfonamides likewise. Some data are given in Table IV.

The polynitro compounds, however, proved admirably adapted for purposes of identification, giving significant depressions in melting points when mixed in any way. But the nitration must be carefully done, for if the nitrating acid acts too vigorously, some of the ethyltrimethylbenzenes are converted to trinitro compounds. It was because of this that Töhl and Tripke[8] reported that dinitroethylmesitylene, obtained by nitrating the hydrocarbon

(7) Smith and Moyle, This Journal, 55, 1680 (1933).

(8) Töhl and Tripke, Ber., 28, 2463 (1895).

TABLE IV

MELTING POINTS OF MIXTURES OF CERTAIN DERIVATIVES
OF POLYALKYLBENZENES

Dibromo Compounds

Ethylmesitylene, %	5-Ethylpseudo-cumene, %	M. p. of mixture, °C.
100	...	59
...	100	60–61
50	50	58.5–59

Sulfonanilides

5-Ethylpseudo-cumene, %	Pseudocumene, %	
100	...	108–110
...	100	145–146
25	75	105–106
50	50	105–107
75	25	104–106

Sulfonamides

5-Ethylpseudo-cumene, %	Pseudocumene, %	
100	...	95–96
...	100	179–180
25	75	163–174
50	50	90–93
75	25	95–99

with fuming nitric acid, melted at 123°. Actually, this compound is a trinitroethyldimethylbenzene, and is not the true dinitroethylmesitylene, which melts at 111°, and which, when mixed with Töhl's 123° nitro compound, melts at 97–102°. Similarly, the ethylpseudocumenes, if nitrated too vigorously, give large amounts of trinitropseudocumene, m. p. 184°. On the other hand, if too mild a nitrating agent is used, nitration will not be complete; thus the method used by one of us[9] for the nitration of durene failed to nitrate exhaustively pseudocumene, mesitylene, 2-, or 4-ethyl-*m*-xylene. After many experiments on the nitration of the pure hydrocarbons, the following procedures were adopted as giving the best yields of polynitro compounds without removing any of the alkyl groups: for prehnitene, 3- and 5-ethylpseudocumenes, and ethylmesitylene, the method of Smith[9] was used; for mesitylene, pseudocumene and the ethyldimethylbenzenes, a mixture of two parts of sulfuric acid and one part of fuming nitric acid was used at 0°. The reaction mixture was then allowed to come to room temperature, after which the nitration was completed by heating for five to ten minutes on the steam-bath. The yields of polynitro compounds were not good (35–50%) even under the best conditions, but the knowledge of the yield of poly nitro compound to be expected from a given hydrocarbon, when combined with careful fractionation of the hydrocarbon mixtures from the rearrangements, made identification of the fractions quite certain and in many cases made it possible to estimate the relative amounts of hydrocarbons present in a mixture of two of them.

5-Ethylpseudocumene (I).—The preparation of this hydrocarbon is given in the previous paper.[6] Certain derivatives of I, however, were of importance in this work; the preparation of these is given below.

5-Ethylpseudocumene Sulfonic Acid.—The hydrocarbon (10 cc.) was shaken vigorously with 10% oleum (10 cc.)

for five minutes. The temperature rose rapidly to 45°, and the hydrocarbon dissolved completely. The solution was stirred slowly into chipped ice (25 g.) and cooled to 10°. The solid was filtered through cloth and sucked as dry as possible. The crude sulfonic acid (15 g., 95%) was dissolved in hydrochloric acid (25 cc.) at 45° or in boiling benzene (50 cc.). The cooled solution deposited white crystals which melted at 72–73°. Klages and Keil[10] give the m. p. as 70–72°. The position of the sulfonic acid group was not determined, but the same sulfonic acid was obtained when the hydrocarbon reacted with chlorosulfonic acid.

5-Ethylpseudocumene Sulfonamide.—The sulfonic acid (1 g.) was converted to the oily sulfonyl chloride by heating on the steam-bath for thirty minutes with phosphorus pentachloride (2 g.) and phosphorus oxychloride (5 cc.). The product was taken up in ether (25 cc.) and the ethereal solution was added to an equal volume of ammonium hydroxide on the hot-plate. After the ether had evaporated, the mixture was cooled and the amide was filtered off. Two crystallizations from alcohol (10 cc.) gave glistening plates melting at 97–98°. Töhl and Karchowski[4] reported that they obtained two sulfonamides, melting at 86 and 153°, respectively. Their results could not be duplicated; only one amide could be obtained and that melted at 97–98°.

Anal. Calcd. for $C_{11}H_{17}O_2NS$: C, 57.15; H, 7.49. Found: C, 57.38; H, 7.58.

The sulfonanilide was prepared by adding a slight excess (10%) of aniline to an ethereal solution of the chloride. The ether was removed, the product was washed with hot, dilute hydrochloric acid and crystallized from dilute alcohol. It melted at 110–111°.

Anal. Calcd. for $C_{17}H_{21}O_2NS$: C, 67.32; H, 6.93. Found: C, 67.34; H, 6.87.

3,6-Dibromo-5-ethylpseudocumene.—The hydrocarbon (3 g.) was sulfonated with 6% oleum (15 g.). The solution was poured onto ice (15 g.) and water was added to bring the volume to 300 cc. Bromine (10 g.) was added gradually, with shaking. The yellow emulsion was allowed to stand for a few hours, then sulfuric acid (5 cc.) was added and the mixture was warmed. After cooling, the solid was removed and crystallized twice from acetone. It melted at 60–61°, and the same substance was obtained when the hydrocarbon was brominated in acetic acid. Töhl and Karchowski[4] reported 218° as the melting point; apparently they mistook tribromopseudocumene (m. p. 225°) for this compound.

Anal. Calcd. for $C_{11}H_{14}Br_2$: C, 42.25; H, 4.57; Br, 52.28. Found: C, 42.04; H, 4.66; Br, 51.81.

3,6-Dinitro-5-ethylpseudocumene, prepared from the hydrocarbon (2 g.) by the method of Smith,[9] was obtained in 37% yield (1.2 g.) after crystallization from alcohol (3 cc.). It melted at 87–88°.

Anal. Calcd. for $C_{11}H_{14}O_4N_2$: C, 55.46; H, 5.88; N, 11.76. Found: C, 55.44; H, 5.90; N, 11.74.

3,6-Diamino-5-ethylpseudocumene Stannichloride.—The dinitro compound (18 g.) was dissolved in acetic acid (100 cc.). To the hot solution was added a hot solution of stannous chloride (140 g.) in hydrochloric acid (160 cc.).

(9) Smith, THIS JOURNAL, **48**, 1420 (1926).

(10) Klages and Keil, *Ber.*, **36**, 1638 (1903).

After the vigorous reaction subsided, the mixture was boiled for ten minutes and then cooled to 0°. The stannichloride (22.1 g., 86%) was filtered, washed with alcohol, then with ether, and dried.

Anal. Calcd. for $C_{22}H_{40}N_4Cl_8Sn$: N, 7.34; Cl, 37.2. Found: N, 7.18; Cl, 37.2.

3,6-Diamino-5-ethylpseudocumene was obtained by treatment of a water suspension of the stannichloride with sodium hydroxide. The suspension was extracted with ether, and, after removal of the ether, the amine was crystallized from ether or ligroin. It melted at 87–88° and was white, although it turned dark rather quickly in the air.

Anal. Calcd. for $C_{11}H_{18}N_2$: C, 74.15; H, 10.11; N, 15.74. Found: C, 74.02; H, 10.48; N, 15.50.

Ethyltrimethylquinone.—The diamine (2 g.) was dissolved in water (20 cc.) and hydrochloric acid (1 cc.). Ferric chloride (8 g.) dissolved in dilute hydrochloric acid (15 cc.) was added. The quinone was formed at once. When crystallized from dilute alcohol, it formed long, yellow needles which had the typical quinone odor and which melted at 41–42°. After sublimation, the quinone melted at 43°.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.27; H, 7.86. Found: C, 74.10; H, 7.69.

3-Ethylpseudocumene[11] (II).—This hydrocarbon was identified as a product of the Jacobsen rearrangement by its boiling point, refractive index, and the m. p. and mixed m. p. of the dinitro compound (79–80°). Certain other derivatives, not given in the previous paper, are described here.

3-Ethylpseudocumene Sulfonic Acid.—The hydrocarbon (10 cc.) was shaken vigorously with concd. sulfuric acid (20 cc.) for two minutes. The temperature rose to 55°. The solution was poured over ice (30 g.) and cooled to 10°. The solid (15 g.) was removed and dissolved in hydrochloric acid (15 cc.) at 40°, and the solution then cooled to 10°. The white solid so obtained melted at 62–64°. Benzene could also be used for recrystallizing it. The position of the sulfonic acid group was not determined.

Anal. Calcd. for $C_{11}H_{16}O_3S$: C, 57.89; H, 7.06; neut. equiv., 228. Found: C, 57.75; H, 7.02; neut. equiv., 227.3.

3-Ethylpseudocumene sulfonamide was prepared by warming the sodium sulfonate (7.5 g.) with phosphorus oxychloride (20 cc.) and phosphorus pentachloride (7 g.) for thirty minutes. The mixture was poured onto ice (50 g.) and extracted with ether (50 cc.). The ethereal solution was added to ammonium hydroxide (50 cc.) on the hot-plate. After removal of the ether, the solid was filtered off and crystallized twice from water. It was white and melted at 154°.

Anal. Calcd. for $C_{11}H_{17}O_2NS$: C, 57.15; H, 7.49. Found: C, 57.1; H, 7.57.

3-Ethylpseudocumene Sulfonanilide.—An ethereal solution of the sulfonyl chloride was prepared as described above, and to it was added a 10% excess of aniline. The ether was evaporated and the product was washed

with hot dilute hydrochloric acid, then crystallized from dilute alcohol. It was white and melted at 118–119°.

Anal. Calcd. for $C_{17}H_{21}O_2NS$: C, 67.32; H, 6.93. Found: C, 67.34; H, 6.87.

Prehnitene (III) was identified by its boiling point, and the m. p. and mixed m. p. of the dinitro compound (176°) and of the sulfonamide (187°).

Pseudocumene (V) was identified by its boiling point, index of refraction, and the m. p. and mixed m. p. of the sulfonic acid-5 (110–111°), trinitro compound (182–184°) and of the tribromo compound (225–226°).

Mesitylene (VIII) was identified by its boiling point, index of refraction, and the m. p. and mixed m. p. of the trinitro compound (232–234°) and of the tribromo compound (224°).

4-Ethyl-*m*-xylene (IV), isolated from the Jacobsen rearrangement of 5-ethylpseudocumene, boiled at 85° under 25 mm., and had $n^{21.5}D$ 1.5008. These values are in good agreement with those found in the literature, Klages and Keil[10] giving: b. p. 67–68° under 12 mm., $n^{16}D$ 1.5033. The hydrocarbon IV gave a trinitro compound, m. p. 127.5–129°,[12] (*Anal.* Calcd. for $C_{10}H_{11}O_6N_3$: N, 15.62. Found: N, 15.5), a tribromo compound, melting at 94–95°[12a] and on oxidation by the method of Schultze[13], IV gave benzene-1,2,4-tricarboxylic acid melting at 210–214°. A mixture of this acid and the acid (m. p. 217°) prepared by oxidation of pseudocumene melted at 213–215°. In addition, the hydrocarbon IV was synthesized from *m*-xylene (see below) and a mixture of the trinitro compound from IV with that from the synthetic hydrocarbon showed no depression in melting point.

2-Ethyl-*m*-xylene (VII).—This hydrocarbon is new. It boiled at 80–83° under 24 mm., $n^{24}D$ 1.5040.

Anal. (Sample of VII from the Jacobsen rearrangement.) Calcd. for $C_{10}H_{14}$: C, 89.55; H, 10.45. Found: C, 89.65; H, 10.37.

Oxidation of VII (1 g.) by boiling it for four hours with a solution of potassium permanganate (9 g.) and sodium hydroxide (5 cc. 10%) in water (180 cc.) produced hemimellitic acid, m. p. 190°.[13] The acid was isolated by acidifying the solution with sulfuric acid, decolorizing with sulfur dioxide, removing the unoxidized material by ether extraction and then by extracting ten times with ethyl acetate. Removal of the ethyl acetate followed by crystallization from dilute hydrochloric acid produced the hemimellitic acid in pure form.

4,5,6-Trinitro-2-ethyl-1,3-dimethylbenzene, m. p. 181°, was obtained by the nitration of VII.

Anal. Calcd. for $C_{10}H_{11}O_6N_3$: C, 44.60; H, 4.04; N, 15.62. Found: C, 44.55; H, 4.10; N, 15.71.

Synthesis of Hydrocarbons IV and VII.—*m*-Xylene (106 g.) was brominated directly with bromine (160 g.) in an ice-bath. The product was washed with alkali, then with water and was dried. Fractionation gave 154 g. (83%) of a mixture of the 2- and 4-bromo-*m*-xylenes, b. p. 102–110° under 24 mm., $n^{18}D$ 1.5490. This mixture of bromo compounds was dissolved in ether (300 cc.) and converted to the Grignard reagent by dropping the solution slowly onto magnesium (22 g.). The reaction was started

(11) See ref. 6 for derivatives and proof of structure of this hydrocarbon.

(12) (a) Stahl, *Ber.*, **23**, 989 (1890); (b) Töhl and Geyger, *ibid.*, **25**, 1534 (1892), give the m. p. of this compound as 127°.

(13) Schultze, *Ann.*, **359**, 143 (1908).

by adding a crystal of iodine, but after starting, it proceeded smoothly and was complete in three hours. The mixture was cooled and ethyl sulfate (309 g.) in ether (200 cc.) was added slowly, with stirring, until the mixture solidified (after about half of the ethyl sulfate was added). After standing for twenty-four hours, the mixture was decomposed with dilute hydrochloric acid. The ether layer was washed thoroughly with water and dried over calcium chloride. After removal of the ether, the residue was boiled for thirty minutes with sodium ethoxide (12 g. of sodium, 200 cc. of alcohol). Ether was added to the cooled solution and the alcohol and alkali were washed out with water. The solution was dried over calcium chloride, the ether was removed and the residue was fractionated. The mixture of IV and VII weighed 37.5 g. (28% overall yield from m-xylene), boiled at 86–87° under 26 mm., n^{20}D 1.5010.

The hydrocarbons were separated as the trinitro compounds, but the nitration of the mixture had to be performed with great care in order to obtain both nitro derivatives. The hydrocarbon mixture (5 g.) was added dropwise to a thoroughly stirred and cooled mixture of fuming nitric acid (10 cc.) and sulfuric acid (20 cc.). After the mixture had come to room temperature, it was heated cautiously at the boiling point for five minutes. The solution was poured over ice, the precipitate was removed and washed once with 5% sodium hydroxide, then twice with *cold* alcohol. The residue was extracted twice with hot alcohol and these solutions were fractionally crystallized. The products were: first crop (0.05 g., 2%), m. p. 180°; second crop (0.2 g., 8%) m. p. 178°; third crop (2.25 g., 90%) m. p. 125–127°. Recrystallization of the first two crops of crystals from alcohol gave 4,5,6-trinitro-2-ethyl-1,3-dimethylbenzene, m. p. and mixed m. p. with the trinitro derivative of VII, 181°. Recrystallization from alcohol of the third crop of crystals gave 2,5,6-trinitro-4-ethyl-1,3-dimethylbenzene, m. p. and mixed m. p. with the trinitro derivative of IV, 129°.

"Polymers" VI and IX.—These products include the insoluble material formed when the sulfonic acids from the Jacobsen rearrangements were dissolved in water, as well as the residue left in the flask after hydrolysis and steam distillation of the sulfonic acid solutions. Both materials were very similar in character, and they constituted 30–35% of the products of the rearrangements. The substances were almost entirely soluble in ether and largely so in acetone and alcohol, and their solutions were opalescent. By repeatedly treating VI (25 g.) with *cold* acetone, a very small amount of a crystalline solid could be extracted (less than 1 g.). After repeatedly crystallizing this from hot acetone, it was white and melted at 173–175°. It may be a hexaalkylbenzene of some sort, but the amount obtained pure was far too small to identify. *Anal.* Found: C, 89.5; H, 10.0. In the same fashion, less than 1 g. of a white crystalline material was isolated from 30 g. of IX. This melted at 185–186°; a mixture of it and the white solid obtained from VI melted at 178–182°. *Anal.* Found: C, 89.5; H, 10.4.

Ethylmesitylene (X).—The preparation of this hydrocarbon is described in the previous paper.[6] Certain derivatives of X, however, were of importance. These are described below.

Ethylmesitylene sulfonic acid was prepared from the hydrocarbon and purified using the methods described above for the sulfonation of 5-ethylpseudocumene, but substituting concd. sulfuric acid for the oleum. The yield was about the same; the melting point was 78–80°, in agreement with the value reported by Klages and Keil.[10]

Ethylmesitylene sulfonamide was prepared from the sulfonic acid, and purified, using the methods described above for the ethylpseudocumene sulfonamides. The white product melted at 131–133°.

Anal. Calcd. for $C_{11}H_{17}O_2NS$: C, 57.15; H, 7.49. Found: C, 56.94; H, 7.64.

Ethylmesitylene sulfonanilide was prepared as described by Klages and Keil.[10] The product, crystallized from alcohol followed by ligroin, melted at 123–124° in agreement with the work of Klages and Keil.

Anal. Calcd. for $C_{17}H_{21}O_2NS$: N, 4.62. Found: N, 4.68.

4,6-Dibromoethylmesitylene.—The hydrocarbon (3 g.) was sulfonated by shaking it with 6% oleum (15 g.) for two minutes. The clear solution was poured onto ice, the volume made up to 300 cc., and bromine (10 g.) was added slowly. The yellow emulsion slowly deposited an oil. Sulfuric acid (5 cc.) was added, the mixture was warmed for a few minutes, and then cooled to 0°. The solid (6 g.) was removed and crystallized first from acetone and then from alcohol. The melting point was 59°, the value given by Klages and Stamm.[14]

Anal. Calcd. for $C_{11}H_{14}Br_2$: C, 42.25; H, 4.57; Br, 52.18. Found: C, 42.04; H, 4.66; Br, 52.30.

4,6-Dinitroethylmesitylene.—The hydrocarbon (5 g.) was dissolved in chloroform (30 cc.) and the solution was stirred thoroughly with sulfuric acid (21 cc.) at 0°. Fuming nitric acid (5.3 g.) was added dropwise during the course of fifteen minutes. The chloroform layer was removed immediately, washed with carbonate, then with water, and dried over calcium chloride. The chloroform was evaporated and the residue crystallized twice from alcohol. The product formed white needles, melting at 109–110°. Repeated crystallization gave a product melting at 111°.

Anal. Calcd. for $C_{11}H_{14}O_4N_2$: C, 55.2; H, 6.3; N, 11.76. Found: C, 54.9; H, 6.4; N, 11.80.

Töhl and Tripke,[8] who nitrated the hydrocarbon with fuming nitric acid, reported that they obtained the dinitro compound, which melted at 123°. This substance is obtained easily by nitrating the hydrocarbon (10 g.) with a mixture of fuming nitric acid (20 cc.) and sulfuric acid (40 cc.) at 0°. The product (11 g.) is difficultly soluble in alcohol, but can be crystallized from a mixture of chloroform and alcohol, when it melts at 123°. When this nitro compound was mixed with the true dinitroethylmesitylene (m. p. 111°), the melting point was 97–102°. Töhl and Tripke reported an analysis for their compound which agreed very well for the values of the true dinitro compound. Nevertheless, this substance is not a dinitro compound, but is a trinitro compound. It was only slightly soluble in hot alcohol, and gave on reduction, not the diamino compound, but a yellow substance melting at 255° which was insoluble in alcohol or chloroform. Analy-

(14) Klages and Stamm, *Ber.*, **37**, 1718 (1904).

sis shows the nitro compound to be a trinitroethyldimethylbenzene.

Anal. Calcd. for $C_{10}H_{11}O_6N_3$: C, 44.6; H, 4.1; N, 15.6. Found: C, 44.3; H, 4.5; N, 15.9.

The substance is not, however, either of the two trinitroethyldimethylbenzenes described in this paper, nor is it trinitroethyl-*p*-xylene. Mixtures of the 123° nitro compound with trinitro-4-ethyl-*m*-xylene (129°), and with trinitroethyl-*p*-xylene (127–128°), melted at 96–100° and 98–110°, respectively. Trinitro-2-ethyl-*m*-xylene, the other trinitro compound available, melts at 181°. The substance may possibly be 3,5,6-trinitro-4-ethyl-*o*-xylene, reported by Stahl[12a] to melt at 121°.

4,6-Diaminoethylmesitylene.—The dinitro compound (1 g., m. p. 110°) was dissolved in hot acetic acid (5 cc.) and to the solution there was added stannous chloride (8 g.) dissolved in hot hydrochloric acid. The vigorous reaction soon subsided, after which the mixture was boiled for ten minutes. The stannichloride separated on cooling, but it dissolved completely when washed with alcohol. The alcoholic solution was combined with the acid filtrate from the stannichloride and an excess of concd. sodium hydroxide was added. The white gelatinous precipitate was removed and crystallized from alcohol (2 cc.) and ligroin (2 cc.). The product formed long white needles which melted at 79–80°.

Anal. Calcd. for $C_{11}H_{18}N_2$: C, 74.15; H, 10.11; N, 15.74. Found: C, 74.30; H, 9.91; N, 15.79.

Ethyl-*p*-xylene was prepared from *p*-xylene by the method described in the previous paper.[6] *p*-Xylene (41.8 g.) was converted to aceto-*p*-xylene (40 g.). The crude product was not purified, but was reduced directly by the Clemmensen method. Ethyl-*p*-xylene (15 g., 28% over-all yield from *p*-xylene) was obtained as an oil, b. p. 81–83° under 25 mm., $n^{20}D$ 1.5020.[15]

Nitration of the hydrocarbon (1 g.) as described for the other ethyldimethylbenzenes gave the trinitro compound,

which after crystallization twice from alcohol (10 cc.) weighed 0.5 g. and melted at 127–128°.[16]

The authors are greatly indebted to Dr. Miles A. Dahlen and E. I. du Pont de Nemours and Company for a generous gift of *m*-xylene which was used in the work described in this and the previous paper.

Summary

1. When subjected to the conditions of the Jacobsen reaction, 5-ethylpseudocumene and ethylmesitylene rearrange, while 3-ethylpseudocumene does not.

2. The two hydrocarbons which rearrange give 3-ethylpseudocumene as the main product, in analogy with the rearrangements of durene and isodurene, all of which rearrange to a 1,2,3,4-tetraalkylbenzene.

3. From 5-ethylpseudocumene, prehnitene, 4-ethyl-*m*-xylene, and pseudocumene were also obtained; from ethylmesitylene, prehnitene, 2-ethyl-*m*-xylene, and mesitylene were also obtained.

4. No hexaalkylbenzenes were identified as rearrangement products, although they may have been formed in small amounts.

5. The formation of a tetramethylbenzene, prehnitene, from ethyltrimethylbenzenes represents a new type of rearrangement.

6. Several derivatives of the starting materials and products are described.

7. Several examples are cited in which mixtures of derivatives of polyalkyl benzenes show little or no depression in melting point.

(15) (a) See ref. 10, where $n^{17}D$ is given as 1.5026; (b) Jacobsen, *Ber.*, **19**, 2516 (1886), gives the b. p. as 185° under atmospheric pressure.

(16) Jacobsen[15b] gives the m. p. as 129°.

The Reaction of Styrene Oxide with Methylmagnesium Iodide

BY CALVIN GOLUMBIC[1] AND D. L. COTTLE

The suggestion that ethylene oxide rearrangements in Grignard reactions are caused by an oxide–magnesium halide bond reaction was made by Bartlett and Berry[2] to account for the formation of methylcyclopentylcarbinol observed by Bedos[3] in reactions of 1,2-epoxycyclohexane and 2-chloro-1-cyclohexanol with methylmagnesium iodide. This explanation served to predict the

formation of 3-methyl-3-pentanol in the reaction of 3-bromo-2-butanol with ethylmagnesium bromide[4] inasmuch as Henry[5] had found that 2,3-epoxybutane reacted with methylmagnesium bromide to produce *t*-amyl alcohol.

Although Fourneau and Tiffeneau[6] found that methyl- and ethylmagnesium bromides reacted with styrene oxide as if it were phenylacetaldehyde, it is impossible to use the explanation in its

(1) Present address, Department of Chemistry, The State University of Iowa, Iowa City, Iowa.

(2) Bartlett and Berry, THIS JOURNAL, **56**, 2683 (1934).

(3) Bedos, *Compt. rend.*, **189**, 255 (1929).

(4) Cottle and Powell, THIS JOURNAL, **58**, 2267 (1936).

(5) L. Henry, *Compt. rend.*, **145**, 406 (1907).

(6) Fourneau and Tiffeneau, *ibid.*, **146**, 698 (1908).