hydroxide solution and evaporated. The residue was crystallized from dilute methanol, m. p. 138–140°. Mixed with the **acetate** of *allo*-pregnanol-3(α)-one-20 (X), m. p. 140–141°, it gave no depression in melting point. When mixed with the acetate of Δ^{16}-*allo*-pregnenol-3(α)-one-20 it melted at 120–132°.

Summary

Dihydroandrosterone was obtained from diosgenin. The intermediates in this preparation are described.

STATE COLLEGE, PENNA. RECEIVED MAY 16, 1940

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Polyalkylbenzenes. XXVII.[1] Preparation of Pure Ethylbenzenes

BY LEE IRVIN SMITH AND CYRUS O. GUSS[2]

Ethylation of benzene to polyethylbenzene has generally been effected by means of the Friedel–Crafts reaction in which ethyl bromide or ethyl chloride and aluminum bromide or aluminum chloride were the reagents used,[3,4,5,6,7] although ethylene[8,9,10] as well as ethanol,[11] ethyl carbonate or diethyl ether[12] have been used in place of the organic halides, and phosphoric acid[13] or phosphorus pentoxide[14] as well as various metallic halides[15,16] have replaced the aluminum halides. Most of the recent work on alkylation to polyethylbenzenes[7,10,11] has indicated that there is a preferential formation of triethylbenzenes. Although tetra-, penta- and hexa-ethylbenzenes were noted, except for the last, the amounts of these substances were small and no study of them was made.

The present work was undertaken in order to devise preparative methods for as many of the pure polyethylbenzenes as possible. It has been found that the ethylation of benzene by ethyl chloride and aluminum chloride occurs quite as readily as does the corresponding methylation, and that it is easily possible to control the alkylation so that the major portion of the product will consist of any desired polyethylbenzenes from tri- to hexa-ethylbenzenes. Moreover, the generalizations with regard to the isomers formed, established in the case of methylations, also hold for the ethylations, namely, that all of the isomers result except the vicinal ones. Thus the triethylbenzene fraction contains no 1,2,3-triethylbenzene, but does contain the other two isomers; the tetraethylbenzene fraction contains no 1,2,3,4-tetraethylbenzene, but the other two isomers are present. Norris and Rubinstein[7] reported that their triethylbenzene fraction consisted only of the 1,3,5-isomer. They used ethyl bromide, while ethyl chloride was used in this work. However, it does not seem likely that the difference in the halide used could account for the complete absence of the 1,2,4-isomer in one case and not in the other. In view of the known orientation effects of alkyl groups, and the peculiar orientations which result when alkylbenzenes are rearranged by aluminum chloride,[17] it is more likely that the absence of the 1,2,4-isomer in the experiments of Norris and Rubinstein was due, not so much to its non-formation as to its rearrangement to the 1,3,5-isomer when in prolonged contact with aluminum chloride.

Good yields of polyethylbenzenes were obtained by passing ethyl chloride into a suspension of aluminum chloride (1.5 moles) in benzene (11.27 moles, 1000 cc.) at 70–75° and at a rate of 2.17 to 2.4 moles per hour. Practically all of the ethyl chloride reacted under these conditions, and the amounts of the different ethylation stages depended upon the amount of ethyl chloride introduced. Using 25–28 moles of the halide, the yield of the polyethylbenzenes was 80–85%, of which 70–75% was triethylbenzenes. When the amount of ethyl chloride was increased to 35

---

[1] XXVI, THIS JOURNAL, **62**, 1349 (1940). The series, started as "Polymethylbenzenes," will be continued henceforth under the more general term "Polyalkylbenzenes."

[2] Abstracted from a thesis by Cyrus O. Guss, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, January, 1940.

[3] Klages, *J. prakt. Chem.*, [2] **65**, 394 (1902).

[4] Gustavson, *ibid.*, [2] **68**, 209 (1903).

[5] Sollscher, *Ber.*, **15**, 1680 (1882).

[6] Wertyporoch and Firla, *Ann.*, **500**, 287 (1933).

[7] Norris and Rubinstein, THIS JOURNAL, **61**, 1163 (1939).

[8] Gattermann, Fritz and Beck, *Ber.*, **32**, 1122 (1899).

[9] Balsohn, *Bull. soc. chim.*, **31**, 540, 635 (1879).

[10] (a) Milligan and Reid, THIS JOURNAL, **44**, 206 (1922); (b) Berry and Reid, *ibid.*, **49**, 3142 (1927); (c) Cline and Reid, *ibid.*, **49**, 3150 (1927); (d) Copenhaver and Reid, *ibid.*, **49**, 3157 (1927).

[11] Norris and Ingraham, *ibid.*, **60**, 1422 (1938).

[12] Norris and Sturgis, *ibid.*, **61**, 1414 (1939).

[13] Ipatieff, Pines and Komarewsky, *Ind. Eng. Chem.*, **28**, 222 (1936).

[14] Malishev, THIS JOURNAL, **57**, 883 (1935).

[15] Wertyporoch, Kowaski and Roeske, *Ber.*, **66**, 1232 (1933).

[16] Grosse and Ipatieff, *J. Org. Chem.*, **1**, 559 (1937).

[17] Nightingale, *Chem. Rev.*, **25**, 329 (1939).

moles, 64% of the product consisted of tetraethylbenzenes, and when about 40 moles of the halide was used, the product consisted of approximately 20% tetraethylbenzenes, 53% pentaethylbenzene, and 20% hexaethylbenzene. When only about 20 moles of the halide was used, ethylation did not proceed appreciably beyond the triethyl stage, which constituted 40% of the reaction product. These ethylations proceeded smoothly and no tarry residues resulted. The reaction mixture separated into two layers, an upper, yellow layer which could be distilled directly, and a dark lower layer containing the aluminum chloride complexes. The lower layer appeared to contain more of the highly ethylated benzenes than the top layer. There was some loss of material due to entrainment by the evolved gases, but this was not large and was not a factor in changing the composition of the product. Thus, by using the same amounts of benzene and aluminum chloride, the same temperatures and reaction times, a change in the amount of ethyl chloride of from 28 to 35 moles altered the composition of the product from 74.8% triethylbenzenes and 7.2% tetraethylbenzenes to 8.4% triethylbenzenes, 64% tetraethylbenzenes and 14% pentaethylbenzene.

The triethylbenzene fraction was separated into its constituents by the method of Dillingham and Reid,[18] who verified and applied an observation of Klages[3] that symmetrical triethylbenzene could be separated from the 1,2,4-isomer by taking advantage of the fact that the former was more difficult to sulfonate than the latter and the sulfonic acid of the former was more readily hydrolyzed than that of the latter. Application of the method to the triethylbenzene fraction obtained in this work led to an 85% recovery of pure triethylbenzenes, of which 85% was the 1,3,5-isomer, 12% was the 1,2,4-isomer, and 3% was a mixture of the two. That no Jacobsen rearrangement occurred during these operations was established by the fact that the pure hydrocarbons could be recovered in good yields when subjected to this procedure.

Aside from one early report by Jacobsen,[19] the literature apparently contains no data on the separation of the tetraethylbenzenes. Jacobsen was not successful in isolating all of the constituents of his mixture, but he did show that the sulfonic acid of *sym*-tetraethylbenzene formed a sparingly soluble sodium salt which was readily purified and from which the hydrocarbon could be regenerated by acid hydrolysis. Smith and Cass[20] have shown that when a mixture of tetramethylbenzenes is cooled to a low temperature, the solid which forms is not only almost entirely durene (m. p. 80°), but that it comprises most of the durene present in the mixture. *sym*-Tetraethylbenzene melts at 10°; hence it was obvious that quite low temperatures would have to be used if any considerable amount of this isomer were to be crystallized from a mixture of tetraethylbenzenes. Nevertheless, by cooling the mixture in a bath of acetone and dry-ice, a large portion of the 1,2,4,5-tetraethylbenzene crystallized and could be filtered off; the filtrate again cooled the same way, yielded a second crop. In this way about 30% of the mixture could be obtained as solid 1,2,4,5-tetraethylbenzene. The filtrate contained about 30% *sym*- and 70% *unsym*-tetraethylbenzene. Complete separation of this mixture into its components was achieved by conversion to the sodium sulfonates, and separation of these by crystallization. It was necessary, however, to sulfonate the mixture by chlorosulfonic acid because the use of sulfuric acid invariably caused the Jacobsen rearrangement to occur. The dioxane sulfotrioxide method of Suter[21] was also tried, but the reagent failed to react with the hydrocarbons. The mixture of sulfonic acids and sulfonyl chlorides was converted into the sodium salts and these were dissolved in the minimum quantity of hot water. On cooling, the sodium sulfonate of 1,2,4,5-tetraethylbenzene crystallized quantitatively, while that of 1,2,3,5-tetraethylbenzene remained in solution. These sulfonates were then hydrolyzed to the hydrocarbons by steam distillation from acid solution at 140°.[22] This method of separating the isomers consistently gave 90% yields of hydrocarbons, about equal amounts of the two isomers resulting. The individual hydrocarbons prepared this way were pure enough for all practical purposes, but extremely pure materials could be obtained by converting the sodium sulfonates to sulfonic acids, precipitating these from sulfuric acid (30–50%) and recrystallizing the sulfonic acids from a mixture of benzene and petroleum ether (b. p. 60–80°) before hydrolysis to the hydrocarbons.

---

[18] Dillingham and Reid, This Journal, **60**, 2606 (1938).

[19] Jacobsen, *Ber.*, **21**, 2814, 2819 (1888).

[20] Smith and Cass, This Journal, **54**, 1609 (1932).

[21] Suter, *ibid.*, **60**, 538 (1938).

[22] Armstrong and Miller, *J. Chem. Soc.*, **45**, 148 (1884).

Experimental Part

Ethylations.—Ethyl chloride from a weighed cylinder[23] was passed through a train consisting of an empty trap, a wash bottle containing sulfuric acid and a second empty trap and then into the reaction vessel. The latter, resting on a steam cone, consisted of a 3-liter round-bottomed flask fitted with a stirrer, reflux condenser, and inlet tube dipping well into the reaction mixture. The evolved gases, together with some benzene vapors, were passed through a second (upright) condenser attached to a suction flask which was cooled, and thence to an absorption tower through which water was recycled. All connections were made with rubber tubing, and tightly fitting cork stoppers were used throughout.

In the early experiments, a second reaction vessel was connected in series with the first one, but when it was found that practically all of the ethyl chloride was absorbed in the first flask, the second flask was eliminated. The conditions under which the experiments were conducted, and general observations made during the experiments, were as follows: (a) the temperature was maintained at about 75°, so that the benzene refluxed gently throughout the experiment, (b) color changes: as the gas was absorbed, the color of the mixture became greenish-yellow, then deep red and finally almost black. As soon as the stirring motor was stopped, the reaction mixture separated into two sharply defined layers; the upper layer was light orange to yellow, and the lower layer, dark red to nearly black. (c) All of the aluminum chloride dissolved soon after the reaction was started; the volume of the mixture increased markedly during the reaction, sometimes nearly doubling. This increase in volume took place largely in the upper layer. (d) By titration of an aliquot of the water cycled through the absorption tower, the approximate amount of hydrochloric acid formed in the reaction was determined. The values found indicated that at least 90% of the ethyl chloride used had reacted. (e) The top layer was removed and distilled without further treatment; the lower layer was poured into iced hydrochloric acid, the oil was removed and then distilled. Both layers showed a beautiful bluish fluorescence, and very little undistillable residue was found in either layer. (f) The quantities of benzene and aluminum chloride were one liter of benzene (11.27 moles) and 200 g. of aluminum chloride (1.5 moles), and these quantities were not varied. The amount of ethyl chloride was varied from 19.3 to 40.2 moles (as measured by the decrease in weight of the cylinder), and the rate of flow was approximately constant; 2.17 to 2.4 moles per hour. (g) In experiments 1 and 2 the second condenser was not used, but the loss of benzene was quite small as shown in expts. 3, 4 and 5 in which the second condenser delivered 0.678, 0.11, and 0.22 mole of benzene, respectively. (h) A column 18 × 1 inches (45.7 × 2.5 cm.), wound with asbestos rope and packed with 6 mm. glass cylinders 1/4 inch (6 mm.) long, was used for the distillation. The distillation rate was 30–50 drops per minute, and a fraction cutter was used so that receivers could be changed without breaking the vacuum. Two fractionations were made; in the first, fractions were taken over a rather wide range in temperature, although by far the major part of each fraction came over within a range of 2–3°. These fractions were then redistilled. The boiling points of the various fractions are given in the tables.[24]

TABLE I

BOILING POINTS OF MIXED POLYETHYLBENZENE FRACTIONS, °C.

Fraction	Pressure, mm.		
	760	20	10
II	181–182	74	60
III	217–218	103	87
IV	248	128	112
V	277	152	135
VI	300	177	153

The results of five ethylation experiments are given in Table II; typical distillation data are given in Tables III–VI.

TABLE II

ETHYLATION OF BENZENE

No. of expt.	1	2	3	4	5
C_6H_6, moles	11.27	11.27	11.27	11.27	11.27
$AlCl_3$, moles	1.5	1.5	1.5	1.5	1.5
C_2H_5Cl, moles	40.2	35.0	19.3	25.3	28.0
HCl evolved, moles	36.74	32.0	17.6	22.8	22.97
Time, hours	16.5	12.0	9.0	10.75	12.0
Temp., °C.	75–80	70–75	70–75	70–75	70–75
Top layer, cc.	1230	1320	845	1150	1195
Bottom layer, cc.	500	480	550	490	500
Vol. of bottom layer after decompn., cc.	140	300	415	330	330
C_6H_6 in trap, moles	...	...	0.687	0.11	0.22
Products formed					
I, g.	...	...	...	...	...
I–II, g.	...	...	221	...	...
II, g.	...	...	...	...	...
II–III, g.	...	4	432	100	200
III, g.	...	118	355	901	968
III–IV, g.	6	105	...	52	32
IV, g.	246	904	...	156	94
IV–V, g.	40	28	...	...	...
V, g.	671	203	...	...	...
VI, g.	250	...	...	...	...
Not distilled, g.	50	48	30	40	...

TABLE III

FRACTIONATION OF PRODUCT FROM EXPT. 2

Product	Temp., °C.	Pressure, mm.	Grams	Volume, cc.
Top layer (volume, 1320 cc.)				
II + III	Up to 93	11	4	5
III	93–104	12	118	140
III + IV	104–110	12	105	122
IV	110–122	11.5	764	883
IV + V	122–130	11.5	28	32
V	130–137	11.5	103	118
Residue	...	...	28	...
Bottom layer (volume, 300 cc.)				
IV	113–130	15–17	140	160
V	130–144	17–13	100	112
Not distilled			20	

---

[23] The authors are greatly indebted to E. I. du Pont de Nemours and Co. for a gift of the ethyl chloride used in this work.

[24] In the tables, Roman numerals refer to mixtures of isomers: II means diethylbenzenes, III means triethylbenzenes, etc.

Table IV

Redistillation of 2770 cc. of Triethylbenzenes (Expts. 2, 3, 4 and 5)

Product	Temp., °C.	Pressure, mm.	Volume, cc.
II + III	60–87	9	171
III	88–90	9	882
III	88–90	9	818
III	90	10.5	847

Table V

Redistillation of 1327 cc. of Tetraethylbenzenes (Expts. 1 and 2)

Product	Temp., °C.	Pressure, mm.	Volume, cc.
IV	110–113	9	81
IV	115–116	11	276
IV	115.5	10.5	160
IV	117	11	165
IV	110–113	9	140
IV	118	11.5	100
IV	116	10.5	323

Table VI

Redistillation of 600-cc. III–IV Fractions (from all Distillations and Redistillations)

Product	Temp., °C.	Pressure, mm.	Volume, cc.
II + III	Up to 90	11	12
III	90–95	11	247
III + IV	95–114	11	172
IV	114–115	11	148

Separation of Pure Isomers. Triethylbenzenes.[18]—The triethylbenzene fraction (200 g.) was stirred with sulfuric acid (400 g.) for three hours at 60–70°. Three layers were formed: a clear top layer (97 g., 112 cc.), a brown middle layer (221 g., 170 cc.) and a dark lower layer (270 g., 155 cc.). The top layer, distilled, gave 94 g. of 1,3,5-triethylbenzene, b. p. 99° under 15.5 mm., 104° under 19 mm. The bottom and middle layers were combined and poured onto ice (600 g.). The resulting solution was steam distilled from a heated flask (thermometer in the acid solution). Up to 125° 1,3,5-triethylbenzene (61 g.) distilled over; from 125 to 140° only a little oil (6 g., mixed triethylbenzenes) came over; slightly above 140°, 1,2,4-triethylbenzene (22 g.) distilled over. The total recovery was 183 g., or 91.5%, of which 155 g. was 1,3,5- and 22 g. was 1,2,4-triethylbenzene. The 1,3,5-triethylbenzene gave a tribromo compound which melted at 100–102°,[4,8,11] while the 1,2,4-triethylbenzene gave a tribromo compound which melted at 86–87°.[25]

Tetraethylbenzenes. 1,2,4,5-Tetraethylbenzene.—Fraction IV (275 cc., b. p. 110–118° under 9–11.5 mm., f. p. −10.5 to −14.5°) was cooled slowly in a bath of acetone and dry-ice until a stiff paste of crystals resulted. This was filtered at −12° in a refrigerated compartment arranged so that operations could be carried out inside. The crystals were pressed and allowed to drain with suction for three hours. The solid consisted of 1,2,4,5-tetraethylbenzene, which melted at 9.5° and which at room temperature amounted to 67 cc. The filtrate was again cooled and the solid was removed. This gave an additional 18 cc. of the hydrocarbon. The total amount of *sym*-tetraethylbenzene was 85 cc. (30.9%); the filtrate amounted to 177 cc., and 13 cc. (4.7%) was lost mechanically. Recrystallization of the 85 cc. of hydrocarbon was accomplished by cooling first to −20° and then to −50° its solution in absolute ethanol (85 cc.) or in ethanol–ether (4:1, 85 cc.). There resulted 78 cc. of pure 1,2,4,5-tetraethylbenzene which melted at 10°.

Separation of the Tetraethylbenzene.—Fraction IV (100 g., 0.526 mole) or the filtrate from the above separation of the *sym* isomer (100 g.) was slowly (thirty minutes) dropped into well stirred and cooled (0–10°) chlorosulfonic acid (100 g., 0.863 mole). The solution darkened and frothed somewhat, and hydrogen chloride was evolved copiously. Excess chlorosulfonic acid was destroyed by slowly pouring the reaction mixture onto crushed ice (about 100–150 g.) and the cold sulfonic acid–sulfonyl chloride mixture (nearly white) was extracted twice with ether. The ether was evaporated and sodium hydroxide (70–80 g.) in water (200–300 cc.) was cautiously added to the residue. The mixture was heated to 95° and more water (250–350 cc.) was added until the salt completely dissolved. The solution at this stage was clear, and light brown or amber in color. The solution was steam distilled for a short time, a necessary step if the sulfonic *acids* were not to be isolated and purified, since the sulfonation reaction was not always complete. A little oil (about 5 cc.) usually distilled over; this was fairly pure *sym*-tetraethylbenzene (m. p. 8–9°). The hot salt solution was poured into a beaker and allowed to cool slowly to room temperature (not lower). The precipitate (sodium *sym*-tetraethylbenzene sulfonate) was filtered off, sucked as dry as possible, transferred to a beaker and stirred twice with a little ether. The ether was filtered off, evaporated and the residue was added to the alkaline filtrate from the sodium salt. The separated salts were converted into sulfonic acids and these were hydrolyzed directly (see below). This procedure led to *sym*-tetraethylbenzene which melted at 8–9°, and to *unsym*-tetraethylbenzene which melted at −22°. When conducted in this way, this method resulted in a 90% recovery of hydrocarbons. Very pure hydrocarbons were obtained by recrystallizing the sodium sulfonate of *sym*-tetraethylbenzene from water before the hydrolysis, or by acidifying the solutions of the sulfonates of either hydrocarbon with excess sulfuric acid (enough to bring the concentration of sulfuric acid to 30–50%), cooling and removing the precipitated sulfonic acids. These were crystallized from a mixture of benzene and petroleum ether, and then hydrolyzed to the hydrocarbons. The results of five separations are given in Table VII.

Table VII

Separation of *sym*- from *unsym*-Tetraethylbenzene

Expt.	1	2	3	4	5
IV mixt., g.	100	100	100	100	100
M. p., °C.	—11.5–12	—13.5	—13.5	(filt.)	...
% *sym* form by curve	49	45	45	30	...
Chlorosulfonic acid, g.	100	100	100	100	100
NaOH, g.	80	80	80	80	50
Water, cc.	550	550	550	600	500
Oil from steam dist. of salts, g.	5	4	12	6	10
Salt of *sym*—IV, g.	...	...	...	27	54
Sym—IV, g.	37	28	28	...	...
M. p., °C.	8–8.5	7.5–8	8–8.5	...	...
Unsym—IV, g.	48	58	51	65	40
M. p., °C.	...	...	...	−22	−22

---

(25) Klages and Keil, *Ber.*, **36**, 1632 (1903).

1,2,4,5-Tetraethylbenzene Sulfonic Acid.—The hydrocarbon (5 g.) was added slowly, with shaking, to chlorosulfonic acid (7 g.). Ice was added carefully and the cold mixture was extracted with ether. The ether was evaporated and sodium hydroxide (4 g.) in water (50 cc.) was added to the residue, which was heated until the sodium sulfonate dissolved. Sulfuric acid was added carefully to the cooled suspension and the sulfonic acid was removed and crystallized from benzene–petroleum ether (b. p. 60–68°). The yield was 6.70–7.12 g. (88.5–94%) of a product which melted at 105–107° after drying in a desiccator over calcium chloride. The sulfonic acid contained one mole of crystal water.

Anal. Calcd. for $C_{14}H_{22}O_3S \cdot H_2O$: C, 58.28; H, 8.39; neut. equiv., 288.2. Found: C, 58.42; H, 8.65; neut. equiv., 284.

Sulfonamide.—Prepared from the acid (1.98 g.) by action of phosphorous oxychloride (10 cc.) and phosphorous pentachloride (4 g.) followed by ammonia, the amide (1.3 g.) crystallized from dilute ethanol, melted at 123–125°.[19,26]

Anal. Calcd. for $C_{14}H_{23}O_2NS$: C, 62.40; H, 8.61. Found: C, 62.25; H, 8.39.

Sulfonanilide.—By substitution of aniline for ammonia in the above procedure, the sulfonic acid (1.0 g.) was converted to the anilide (1 g.) which crystallized in needles from dilute ethanol. It melted at 107–108°.

Anal. Calcd. for $C_{20}H_{27}O_2NS$: C, 69.52; H, 7.88. Found: C, 69.45; H, 7.92.

Hydrolysis to the Hydrocarbon.—The pure sulfonic acid (50 g., m. p. 105–107°) was added to sulfuric acid (300 cc., 50%) and steam was passed through while the temperature was gradually increased (thermometer in the solution). Hydrolysis was slow at 120°, but quite rapid at 140°. The residue was clear, and colored only slightly. The distillate contained 32.5 g. (98.5%) of hydrocarbon which melted at 10°.

Anal. Calcd. for $C_{14}H_{22}$: C, 88.34; H, 11.66. Found: C, 87.96; H, 11.61.

Action of Dioxane Sulfotrioxide.[21]—Sulfur trioxide (16 g.) was passed, with cooling, into dry dioxane (22 g.) in dry carbon tetrachloride (75 cc.). To the resulting white suspension was added *sym*-tetraethylbenzene (10 g.) and the mixture was allowed to stand at room temperature for three days with frequent shaking. The reaction mixture was poured over ice and the carbon tetrachloride layer was removed. From it was obtained 9 g. of unchanged hydrocarbon. Nothing separated from the aqueous layer when it was made strongly acid (50%) with sulfuric acid.

1,2,3,5-Tetraethylbenzene Sulfonic Acid.—Prepared from the hydrocarbon as described for its isomer above, and purified by crystallization from benzene–petroleum ether, this sulfonic acid likewise contained a molecule of crystal water. After drying in a desiccator over calcium chloride, it melted at 97–99°; when mixed with its isomer (m. p. 105–107°), it melted at 80–87°.

Anal. Calcd. for $C_{14}H_{23}O_3S \cdot H_2O$: C, 58.28; H, 8.39; neut. equiv., 288.2. Found: C, 58.15; H, 8.35; neut. equiv., 283.

Sulfonamide.—The amide, prepared as above and crystallized from dilute ethanol, melted at 56–57°. It was necessary to crystallize it from dilute solutions, otherwise it separated as an oil.

Anal. Calcd. for $C_{14}H_{23}O_2NS$: C, 62.40; H, 8.61. Found: C, 61.97; H, 8.50.

Sulfonanilide.—Prepared and purified as above, the anilide melted at 78–79°.

Anal. Calcd. for $C_{20}H_{27}O_2NS$: C, 69.52; H, 7.88. Found: C, 69.86; H, 7.84.

Hydrolysis to the Hydrocarbon.—The hydrolysis was carried out as described above. Hydrolysis was slow at 120°, rapid at 140°. From 84 g. of the sulfonic acid (m. p. 97–99°) there resulted 54 g. (98%) of hydrocarbon which melted at −21°.

Anal. Calcd. for $C_{14}H_{22}$: C, 88.34; H, 11.66. Found: C, 88.35; H, 12.07.

Summary

1. The ethylation of benzene by ethyl chloride and aluminum chloride has been studied, and efficient procedures have been developed whereby the alkylation may be conducted so as to give mainly tri-, tetra-, penta- or hexa-ethylbenzenes.

2. The triethylbenzene fraction so obtained consisted of about 85% 1,3,5-triethylbenzene and 15% 1,2,4-triethylbenzene. These isomers were best separated by the method of Dillingham and Reid, which gave over 90% recovery of the separated hydrocarbons.

3. An efficient method for the separation of the two tetraethylbenzenes present in approximately equal amounts in this fraction was devised. This method resulted in better than 90% recovery of the separated hydrocarbons.

4. In these ethylations, no vicinal isomers, 1,2,3-triethylbenzene or 1,2,3,4-tetraethylbenzene, were formed. In this respect, the ethylations paralleled the methylations previously studied.

5. The sulfonic acids, sulfonamides and sulfonanilides of the two tetraethylbenzenes have been prepared and characterized.

MINNEAPOLIS, MINNESOTA RECEIVED MARCH 2, 1940

---

[26] Jacobsen (Ref. 19) reports the m. p. as 122°.