the supposition that sodium butylate is a specially active condensing agent. As a whole the experiments show that the salts are efficient condensing agents. Unfortunately they are also dehydrating agents and much of the octanol may be destroyed. It is probable that at a lower temperature and with a shorter time considerable condensation could be attained without much dehydration. Comparing runs 3 to 8, it is seen that potassium and rubidium salts are equally effective while the sodium is less so. Calcium butyrate produced little condensation and curiously the octanol fraction boiled about 10° lower than with the other salts. In run 11 there was excessive dehydration, due to the high temperature. Runs 12 to 14 show that a much larger amount of the catalytic salt produces a good yield of octanol with little dehydration. In run 13 the tube was known to have leaked; the octanol represented a yield of 40% calculated on the recovered oil. A seven-hour run at 350° of propyl alcohol with 25% of potassium propionate gave 10% condensation. The efficiency of potassium salts may be due to their greater solubility.

Experimental

The caustic oxidations runs were made in a 3-in. (8-cm.) outside diameter chrome–vanadium steel tube of 800-cc. capacity. This was rocked through a small angle. It was electrically heated and the temperature was taken with a thermocouple. The condensation runs were made in a larger tube of the same kind. The charge was 1000 g. of dry butanol. Water was added to the reaction product to dissolve the salts and the oily layer separated, dried and fractionated.

Summary

1. A primary alcohol heated with sodium or potassium hydroxide is converted into the corresponding fatty acid salt; the alkali is used up completely if the alcohol is in excess.

2. The presence of water is advantageous; it prevents condensation of the alcohol with itself and darkening of the product.

3. Potassium and sodium salts of fatty acids are efficient catalysts for condensing two molecules of an alcohol into one of a higher.

The Action of Aluminum Chloride on Aromatic Hydrocarbons. I.[1] The 1,3-Dimethyl-4-butylbenzenes

By Dorothy Nightingale[2] and Lee Irvin Smith

Anhydrous aluminum chloride brings about the migration of alkyl groups in aromatic hydrocarbons. Baddeley and Kenner[3] reported that when 1,3,4-tri-n-propylbenzene was warmed with aluminum chloride at 100°, the 1,3,5-tri-n-propyl isomer was formed, along with the lower and higher alkylated benzenes. They state that there can be little doubt that the normal character of the migrating propyl group was preserved, but offer no experimental proof for this statement. Smith and Perry[4] found that 1,3-dimethyl-4-t-butylbenzene warmed with aluminum chloride gave a 45% yield of the 1,3,5-isomer.

To study further the effect of aluminum chloride on 1,3,4-hydrocarbons, and to determine whether or not there is isomerization of the migrating radical, the four 1,3-dimethyl-4-butylbenzenes were chosen for this investigation.

It is well known that aluminum chloride and other metal halides cause isomerization of the alkyl radical, especially if the alkyl halide is primary. Shoesmith and McGechen[5] made a careful study of the reaction between the butyl halides and toluene and found that n-butyl chloride gave a 75% yield of m-s-butyltoluene and 25% of the p-isomer, rather than an o–p mixture. With isobutyl bromide, the m:p ratio of t-butyltoluenes was 70:30.

In the syntheses of trialkylbenzenes from benzene or from m-dialkylbenzenes, by procedures involving the use of aluminum chloride as a catalyst, the principal product has the 1,3,5-configuration rather than 1,3,4- as would be expected. In

(1) Polymethylbenzenes. XXII. Paper XXI, This Journal, 60, 652 (1938).

(2) Honorary Fellow, 1938. Present address: Department of Chemistry, University of Missouri, Columbia, Missouri.

(3) Baddeley and Kenner, J. Chem. Soc., 303 (1935).

(4) Moyle and Smith, J. Org. Chem., 2, 114 (1937).

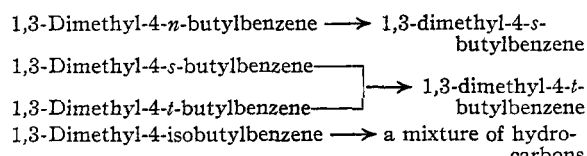(5) Shoesmith and McGechen, J. Chem. Soc., 2231 (1930).

these cases, either the alkyl groups in the meta position do not exert their usual directing influence or, as suggested by Moyle and Smith,[4] and by Schorger,[5a] a 1,3,4-hydrocarbon is first formed and this is rearranged to the 1,3,5-hydrocarbon by the aluminum chloride. Bauer's[6] synthesis of 1,3-dimethyl-5-t-butylbenzene from m-xylene and t-butyl chloride is an early and well-known example of this effect. In the reaction between m-xylene and acyl chlorides, however, the product is always a 1,3-dimethyl-4-acylbenzene.

Schorger[5a] treated cymene with aluminum chloride and other metal halides under various conditions, and isolated benzene, toluene, m-xylene, and 1-methyl-3,5-diisopropylbenzene from the products of the reaction.

Moore and Egloff[7] report that cumene and aluminum chloride at 150° gave, among other hydrocarbons, a 26% yield of xylenes. This they attribute to the decomposition of the isopropyl group.

The 1,3-dimethyl-4-R-benzenes can be prepared from m-xylene and an alcohol in the presence of 70–85% sulfuric acid, according to the general procedure outlined by Kirrmann and Graves[8] or by the method of Meyer and Bernhauer.[9] These methods can be used only when the desired R is secondary or tertiary. If R is to be primary, the 1,3,4-hydrocarbons can be prepared by the reduction of the corresponding 4-acyl-m-xylenes.

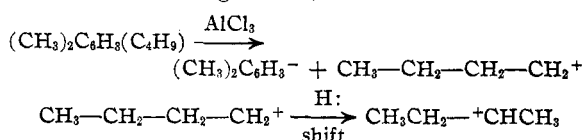The principal changes involved when the 1,3-dimethyl-4-butylbenzenes are treated with aluminum chloride are as follows

1,3-Dimethyl-4-n-butylbenzene ⟶ 1,3-dimethyl-4-s-butylbenzene

1,3-Dimethyl-4-s-butylbenzene ⟶
1,3-Dimethyl-4-t-butylbenzene ⟶ 1,3-dimethyl-4-t-butylbenzene

1,3-Dimethyl-4-isobutylbenzene ⟶ a mixture of hydrocarbons

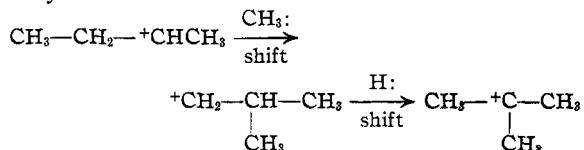Other products of the reaction are m-xylene and presumably higher alkylated benzenes.

Results with 4-propyl- and 4-amyl-1,3-dimethylbenzenes, which will be published later, indicate that in these and other related cases there is also a rearrangement within the alkyl group when this group migrates.

If it may be assumed that the metal chloride in some way leads to the formation of butyl ions, the

isomerization of the n-butyl radical may be interpreted in terms of Whitmore's[10] theory of intramolecular rearrangements, as follows

$$(CH_3)_2C_6H_3(C_4H_9) \xrightarrow{AlCl_3}$$
$$(CH_3)_2C_6H_3^- + CH_3—CH_2—CH_2—CH_2^+$$
$$CH_3—CH_2—CH_2—CH_2^+ \xrightarrow[shift]{H:} CH_3CH_2—^+CHCH_3$$

The isomerization of the s-butyl radical from 1,3-dimethyl-4-s-butylbenzene could take place similarly

$$CH_3—CH_2—^+CHCH_3 \xrightarrow[shift]{CH_3:}$$
$$^+CH_2—CH—CH_3 \xrightarrow[shift]{H:} CH_3—^+C—CH_3$$
$$\qquad\ \ |\qquad\qquad\qquad\qquad |$$
$$\qquad CH_3 \qquad\qquad\qquad\quad CH_3$$

This leads to the question: if an s-butyl ion is formed from an n-butyl ion, why is it not further isomerized to yield finally a t-butyl ion? It is of course possible that an ionic mechanism does not apply to this type of rearrangement.

Experimental[11]

The procedure of Kirrmann and Graves[8] was used for the preparation of the 1,3-dimethyl-4-s-butyl- and 4-t-butylbenzenes. A large excess of m-xylene always was used to minimize the formation of higher alkylated benzenes. The butyryl m-xylenes were reduced according to Clemmensen's[12] directions.

The melting points of the two t-butyl-m-xylenes were determined by means of cooling curves. The other hydrocarbons became viscous at about −60° and set to a glass around −80°.

1,3-Dimethyl-4-t-butylbenzene.—The pure m-xylene (375 cc.) and t-butyl alcohol (55 cc.) were mixed and the flask placed in water cooled with a little ice. A mixture of 525 cc. of concd. sulfuric acid and 110 cc. of water was added during an hour while the solution was stirred mechanically. The stirring was continued for fourteen hours at room temperature. The xylene layer was separated, washed repeatedly with water and dilute alkali, dried and vacuum distilled, using a column packed with single turn glass helices: yield, 38 g. (41%) of hydrocarbon, b. p. 86° (12 mm.); d^{20}_{20} 0.8634; n^{25}D 1.4909; m. p. −31°.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.81; H, 11.19. Found: C, 88.66; H, 11.30.

Under these same conditions, 200 cc. of m-xylene and 30 cc. of isobutyl alcohol gave 10 g. (21%) of 1,3-dimethyl-4-t-butylbenzene.

1,3-Dimethyl-4-s-butylbenzene.—This hydrocarbon was prepared in the same way from 375 cc. of m-xylene and 60 cc. of s-butyl alcohol: yield, 53 g. (50%), b. p. 84° (8 mm.); n^{25}D 1.4939; d^{20}_{20} 0.8680.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.81; H, 11.19. Found: C, 88.66; H, 11.07.

(5a) Schorger, THIS JOURNAL, **39**, 2671 (1917).

(6) Bauer, *Ber.*, **24**, 2840 (1891).

(7) Moore and Egloff, *Met. Chem. Eng.*, **17**, 61 (1917).

(8) Kirrmann and Graves, *Bull. soc. chim.*, [5] **1**, 1494 (1934).

(9) Meyer and Bernhauer, *Monatsh.*, **53**, 721 (1928).

(10) Whitmore, THIS JOURNAL, **54**, 3275 (1932).

(11) Microanalyses by J. W. Opie.

(12) Clemmensen, *Ber.*, **46**, 1838 (1913).

The yield of this hydrocarbon when n-butyl alcohol was used was 6%.

1,3-Dimethyl-4-n-butylbenzene.—The 4-n-butyryl-m-xylene was prepared by the usual Friedel–Crafts procedure from 146 cc. of m-xylene, 400 cc. of carbon disulfide, 292 g. of aluminum chloride and 158 g. of n-butyric anhydride. The yield of pure ketone was 116 g. (53%), b. p. 118° (8 mm.).

The ketone (50 g.) was reduced to the hydrocarbon by the Clemmensen[12] method: yield 23 g., b. p. 96° (8 mm.); d^{20}_{20} 0.8728; n^{25}D 1.4972.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.81; H, 11.19. Found: C, 89.02; H, 11.49.

1,3-Dimethyl-4-isobutylbenzene.—The 4-isobutyryl-m-xylene was prepared as above from 146 g. of m-xylene, 100 g. of isobutyryl chloride, 133 g. of aluminum chloride and 400 cc. of carbon disulfide. The yield of pure ketone was 127 g. (72%), b. p. 121° (14 mm.).

The ketone (90 g.) was reduced by the Clemmensen[12] method: yield of 1,3-dimethyl-4-isobutylbenzene was 44 g. (49%); b. p. 96° (15 mm.); d^{20}_{20} 0.8704; n^{25}D 1.4974.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.81; H, 11.19. Found: C, 89.12; H, 10.89.

1,3-Dimethyl-5-s-butylbenzene.—This hydrocarbon was prepared by the procedure of Shoesmith and McGechen[5] from 150 g. of m-xylene, 46 g. of n-butyl chloride, and 30 g. of aluminum chloride: yield 40 g. (50%); b. p. 98° (15 mm.); d^{20}_{20} 0.8631; n^{25}D 1.4920.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.81; H, 11.19. Found: C, 89.07; H, 11.10.

1,3-Dimethyl-5-t-butylbenzene was obtained in 50% yield from m-xylene and t-butyl chloride at room temperature, d^{20}_{20} 0.8671; m. p. −21.5°; n^{25}D 1.4935.

The trinitro derivatives were all prepared by adding 1 cc. of the hydrocarbon to 5 cc. of a nitrating mixture (30 cc. nitric acid, sp. gr. 1.5 and 42 cc. concd. sulfuric acid) cooled in ice. After standing for a time the mixture was poured onto ice. Yields were good with the exception of the 4-n-hydrocarbon. The 4-isobutyl hydrocarbon has not yielded a solid nitro derivative.

1,3-Dimethyl-hydrocarbon	M. p., °C.	Trinitro derivative[a] %C Found	%H
4-n-Butylbenzene	91	48.76	5.40
4-s-Butylbenzene	107	48.89	5.10
4-t-Butylbenzene	112	48.98	5.23
5-s-Butylbenzene	97	48.51	5.30
5-t-Butylbenzene	113[b]		

[a] Calcd. for $C_{12}H_{15}N_3O_6$: C, 48.45; H, 5.08.   [b] Bauer[6] reports 110°.

With the exception of the trinitro derivative of 1,3-dimethyl-5-s-butylbenzene, all of these trinitro derivatives crystallize from alcohol as needles. The crystals of the 5-s-hydrocarbon are fibrous.

Rearrangement with Aluminum Chloride.—The aluminum chloride was added directly to the hydrocarbon, and the mixture warmed on the steam-bath. There was some evolution of a gas, but no attempt was made at this time to identify gaseous decomposition products. After heating, the mixture was poured onto ice, extracted with ether and vacuum distilled. In all cases fraction I proved to be largely m-xylene. Some additional m-xylene or any lower alkylated benzenes are probably lost at the low pressures used. No one hydrocarbon was isolated from the mixture in fraction IV since it was not possible to obtain a cut of constant boiling point from the small amount of material.

1,3-Dimethyl-4-n-butylbenzene.—The hydrocarbon (37 g.) was warmed with aluminum chloride (8 g.) for four hours on a steam-bath. The products of the reaction were fractionated at 16 mm.: (I) 3.5 g. 45–50°; (II) 5.5 g. 50–105°; (III) 7 g. 105°; (IV) 10 g. 105–145°.

Fraction III, on slow distillation, came over at 101° (16 mm.); d^{20}_{20} 0.8650; n^{25}D 1.4928. The trinitro derivative of III crystallizes in fibers, m. p. 97°. The trinitro derivative of an authentic sample of 1,3-dimethyl-5-s-butylbenzene also crystallizes in fibers, m. p. 97°, and a melting point of mixtures of the two products is 97°. The rearrangement product is therefore 1,3-dimethyl-5-s-butylbenzene.

1,3-Dimethyl-4-s-butylbenzene.—The hydrocarbon (37 g.) was warmed with the aluminum chloride (8 g.) for two and one-half hours. The reaction products were fractionated at 17 mm.: (I) 3.5 g. 44°; (II) 1.0 g. 44–91°; (III) 16 g. 91°; (IV) 5 g. 91–145°.

Fraction III on slow distillation came over at 91° (17 mm.); d^{20}_{20} 0.8664; n^{25}D 1.4938; f. p. −23°. Its trinitro derivative melts at 113°, and the melting point of a mixture of this trinitro derivative and trinitro-1,3-dimethyl-5-t-butylbenzene is 113°. The freezing point of a mixture of III with an authentic sample of 1,3-dimethyl-5-t-butylbenzene (f. p. −21.5°) is −21.5°. These data indicate definitely that this rearrangement product is 1,3-dimethyl-5-t-butylbenzene.

1,3-Dimethyl-4-t-butylbenzene.—The hydrocarbon (48 g.) was warmed with aluminum chloride (10 g.) for three and one-quarter hours. The product was fractionated at 8 mm.: (I) 3 g. 32°; (II) 2 g. 32–75°; (III) 15 g. 75°; (IV) 7 g. 75–145°.

Fraction III, on slow distillation, came over at 76° (8 mm.), d^{20}_{20} 0.8651, n^{25}D 1.4935; f. p. −20.5°. Its trinitro derivative melts at 113°, and the melting point of a mixture of this trinitro derivative and the trinitro derivative of 1,3-dimethyl-5-t-butylbenzene synthesized by the Friedel–Crafts reaction is also 113°.

1,3-Dimethyl-4-isobutylbenzene.—The hydrocarbon (50 g.) was warmed with 10 g. of aluminum chloride for three hours. The reaction product when fractionated at 16 mm. yielded 4 g. of m-xylene and 40 g. of complex mixture distilling at 90–145°. This reaction will require further study.

The study is being continued.

Summary

The four 1,3-dimethyl-4-butylbenzenes and 1,3-dimethyl-5-s-butylbenzene have been synthesized, and crystalline trinitro derivatives made of them with the exception of the 1,3-dimethyl-4-isobutylbenzene.

The 1,3-dimethyl-4-t-butylbenzene and the 1,3-dimethyl-4-s-butylbenzene both undergo rearrangement on treatment with aluminum chloride to give 1,3-dimethyl-5-t-butylbenzene. The identity of the 1,3,5-hydrocarbon formed by these rearrangements was established by means of melting points of mixtures of the trinitro derivatives and by freezing points of mixtures of rearrangement product with an authentic sample of the

1,3,5-hydrocarbon synthesized by the Friedel–Crafts reaction.

The 1,3-dimethyl-4-isobutylbenzene on treatment with aluminum chloride yields a mixture of hydrocarbons.

The 1,3-dimethyl-4-n-butylbenzene and aluminum chloride yields 1,3-dimethyl-5-s-butylbenzene.

Phenylpropiol-4-chlorothioanilide

BY DAVID E. WORRALL AND EDWARD LAVIN

The thioamide obtained by the condensation of sodium phenylacetylene with phenyl isothiocyanate has been shown to react characteristically[1] with hydroxylamine and hydrazine. Since the resulting isoxazole or pyrazole, as the case may be, contains replaceable hydrogen both in the heterocyclic ring (position 4) and in the aniline ring, the reaction has been found useful for the synthesis of certain derivatives.[2] The present investigation is concerned with the reactions of chlorinated thioanilides of this series.

Experimental

Phenylpropiol-4-chlorothioanilide (I).—To 0.25 gram mole of sodium phenylacetylene suspended in ether was added an equivalent amount of p-chlorophenyl isothiocyanate. The mixture, after standing overnight, was worked up in the customary manner, yielding after thorough washing with cold alcohol approximately 50 g. of material. A small portion was recrystallized from alcohol, separating as yellow plates, m. p. 138–139° with decomp.

Anal. Calcd. for $C_{15}H_{10}ClNS$: C, 66.3; H, 3.7. Found: C, 66.4; H, 3.5.

bis-**Phenylpropiol-4-chloroanilide.**—Heat alone even at 100° changed I into a black tar that on cooling hardened into a glossy black resin. The dimer obtained by heating an ether solution of I in the presence of alkali, separated after several hours as a dark green crystalline mass. It was thoroughly washed with hot alcohol; m. p. 245–246°, dec.

Anal. Calcd. for $(C_{15}H_{10}ClNS)x$: C, 66.3; H, 3.7. Found: C, 66.3; H, 3.9.

A poor yield of the dibromide of I was obtained from the polymer suspended in chloroform. Yellow crystals melting with decomposition at 229–230° separated.

Anal. Calcd. for $C_{15}H_{10}Br_2ClNS$: C, 41.6; H, 2.5. Found: C, 41.3; H, 2.6.

(1) Worrall, THIS JOURNAL, **59**, 933 (1937).

(2) Worrall, *ibid.*, **60**, 1198 (1938).

3-(4-Chloroanilino)-5-phenylisoxazole (II).—Using an excess of hydroxylamine with 10 g. of I, a product was obtained that eventually, after repeated crystallizations from alcohol, formed nearly colorless plates, m. p. 166–167°; yield 1.5–2 g.

Anal. Calcd. for $C_{15}H_{11}ClN_2O$: C, 66.5; H, 4.1. Found: C, 66.8; H, 4.6.

1-Phenacyl-5-chlorobenzothiazole.—A small amount of insoluble material separated from the isoxazole preparation. It crystallized from glacial acetic acid as scarlet needles, melting with decomposition at 192–193°.

Anal. Calcd. for $C_{15}H_{10}ClNOS$: C, 63.1; H, 3.5. Found: C, 62.6; H, 3.5.

3-(2-Bromo-4-chloroanilino)-4-bromo-5-phenylisoxazole.—To 0.5 g. of II dissolved in warm chloroform was added a slight excess of bromine. Tufts of white needles separated on cooling, m. p. 133–134°.

Anal. Calcd. for $C_{15}H_9Br_2ClN_2O$: Br, 37.3. Found: Br, 37.5.

3-(2,4-Dichloroanilino)-4-chloro-5-phenylisoxazole.—Dry air was blown through a chloroform solution of II which previously had been saturated with chlorine. The residue separated from ligroin in the form of needles slightly discolored; m. p. 95–96°.

Anal. Calcd. for $C_{15}H_9Cl_3N_2O$: Cl, 31.4. Found: Cl, 31.2.

3-(2-Nitro-4-chloro)-4-nitro-5-phenylisoxazole.—A small portion of II dissolved in nitric acid and precipitated by water crystallized from glacial acetic acid as pale yellow plates, m. p. 165–166°.

Anal. Calcd. for $C_{15}H_9ClN_4O_5$: C, 50.0; H, 2.5. Found: C, 49.9; H, 2.5.

3-(4-Chloroanilino)-5-phenylpyrazole (III) was prepared from 10 g. of I using two equivalents of hydrazine. The crude product was heated with ligroin, thus removing much of the color, after which it was crystallized several times from alcohol as cream-colored needles, m. p. 174–175°; final yield, 2.4 g.

Anal. Calcd. for $C_{15}H_{12}ClN_3$: C, 66.8; H, 4.5. Found: C, 66.9; H, 4.4.