[CONTRIBUTION FROM CHEMICAL LABORATORIES OF TEMPLE UNIVERSITY]

The Action of Aluminum Chloride on *n*-Butylbenzene

BY R. E. KINNEY AND LYLE A. HAMILTON

RECEIVED AUGUST 31, 1953

n-Butylbenzene, when treated with aluminum chloride at 100°, forms benzene and di-*n*-butylbenzene. The recovered di-*n*-butylbenzene fraction yields *n*-butylbenzene as the only product when treated with aluminum chloride and excess benzene. No isomerization of *n*-butyl groups was observed. The di-*n*-butylbenzene formed was at least 90% meta with only minor amounts of ortho or para isomers.

Early work on the aluminum chloride catalyzed disproportionation of *n*-alkylbenzenes indicated that the alkyl groups are not isomerized and that *m*-substituted benzenes are formed in predominant amount. Heise and Tohl[1] report that *n*-propylbenzene and aluminum chloride yield benzene, *m*- and *p*-di-*n*-propylbenzene and unchanged *n*-propylbenzene, with no isomerization of the propyl groups taking place. Baddeley and Kenner[2] found that treatment of *p*-di-*n*-propylbenzene with aluminum chloride at 100° yielded *n*-propylbenzene, *m*-di-*n*-propylbenzene and 1,3,5-tri-*n*-propylbenzene, plus some unchanged *p*-di-*n*-propylbenzene. With *m*-di-*n*-propylbenzene, essentially unchanged *m*-derivative was recovered. The accuracy of this work was held in doubt by later investigators[3] because of insufficient characterization of products and because of the relatively drastic conditions used. In alkylations with *n*-propyl or *n*-butyl chlorides and aluminum chloride, *n*-alkylbenzenes are principal products only in the cold.

It seemed desirable to clarify this situation and to determine the products of the disproportionation in an unambiguous manner. Infrared and mass spectrometer analytical techniques seemed particularly suitable.

n-Butylbenzene of high purity was available from the Phillips Petroleum Co. and pure samples of the four isomeric butylbenzenes were available as spectrographic pattern samples.

n-Butylbenzene was heated with 20% by wt. of aluminum chloride for three hours at 100°. Fractionation of the products yielded benzene, monobutylbenzene, dibutylbenzene and a higher boiling residue. The recovered monobutylbenzene was shown by mass spectrometer analysis to be over 99 mole % *n*-butylbenzene. Identification of the dibutylbenzene fraction was undertaken by means of infrared analysis. Initial results indicated that only di-*n*-butylbenzene was present, and that the orientation was all or predominantly meta. Fortunately, an authentic[4] sample of *m*-di-*n*-butylbenzene was available for comparison. It was thus established that the dibutylbenzene formed in the disproportionation reaction was at least 90% *m*-di-*n*-butylbenzene.

In order to confirm further the fact that isomerization of the butyl groups did not occur, a sample of the dibutylbenzene fraction from the disproportionation was converted back to monobutylbenzene by reaction with excess benzene and aluminum chloride at 85°. In this way 75 mole % of the dibutylbenzene was converted to monobutylbenzene. Mass spectrometer analysis showed this to be over 99 mole % *n*-butylbenzene. It is thus definitely established that no rearrangement of migrating alkyl groups took place in the disproportionation reaction or in the reaction of dibutylbenzene with benzene.

It is probable that transfer of the butyl groups is not by means of a free carbonium ion, since isomerization of the latter to the secondary or *t*-butyl configuration should take place under the conditions used. McCaulay and Lien[5] found that no isomerization of alkyl groups occurred in the disproportionation of alkylbenzenes with hydrogen fluoride–boron trifluoride catalyst. They suggest that the transfer of alkyl groups takes place by a bimolecular displacement mechanism in which the migrating group forms a partial bond with a second aromatic ring before the bond with the first ring is broken. It seems likely that a similar mechanism is operative in the case of disproportionation with aluminum chloride catalyst.

Lien and McCaulay[6] find using a hydrogen fluoride–boron trifluoride catalyst with boron trifluoride in excess, that *m*-diethylbenzene and benzene are the only products from the disproportionation of ethylbenzene at 0°. This they attribute to the formation of a complex between *m*-diethylbenzene and boron trifluoride. With a deficiency of boron trifluoride some ortho and para isomers are formed together with 60–75% of the meta isomer.

Our data are insufficient to indicate whether the predominant meta isomer formation found with aluminum chloride, over 90% meta, can be attributed to complex formation of the meta isomer with aluminum chloride as might be expected if the mechanism is similar to that suggested by Lien for the hydrogen fluoride–boron trifluoride system.

Experimental

n-Butylbenzene (Phillips, Pure Grade) was used. It had a boiling point of 183.6° and mass spectrometer analysis indicated 99.6 mole % of *n*-butylbenzene and 0.3 mole % of *s*-butylbenzene.

Experiment A.—A mixture of 202.5 g. of *n*-butylbenzene and 40.0 g. of aluminum chloride (Baker and Adamson, reagent grade, anhydrous, sublimed) was stirred for three hours at 100°. It was observed that two layers were formed, the lower being of relatively small volume and very dark in color. At the end of the reaction period the product was poured over cracked ice; the organic layer was separated, washed with water, and dried over anhydrous calcium

---

[1] R. Heise and A. Tohl, *Ann.*, **270**, 155 (1892).

[2] G. Baddeley and J. Kenner, *J. Chem. Soc.*, 303 (1935).

[3] (a) D. V. Nightingale and L. J. Smith, THIS JOURNAL, **61**, 101 (1939), (b) D. V. Nightingale, *Chem. Revs.*, **25**, 329 (1939); (c) D. V. Nightingale and B. Carton, THIS JOURNAL, **62**, 280 (1940).

[4] Sample supplied by Dr. G. Forrest Woods, University of Maryland, data given in *ibid.*, **73**, 5603 (1951).

[5] D. A. McCaulay and A. P. Lien, *ibid.*, **75**, 2411 (1953).

[6] A. P. Lien and D. A. McCaulay, *ibid.*, **75**, 2407 (1953).

chloride. A total of 192.8 g. of hydrocarbon was recovered at this step.

Careful fractionation of this hydrocarbon gave 15.2% of benzene, 45.2% of *n*-butylbenzene, b.p. 96.5–97.5° at 50 mm. (99.4 mole % *n*-butylbenzene and 0.6 mole % *s*-butylbenzene by mass spectrometer analysis), 27.7% of dibutylbenzene, b.p. 160–162° at 50 mm. (at least 90 mole % *m*-di-*n*-butylbenzene), and 11.9% of a higher boiling residue.

Experiment B.—A mixture of 50.7 g. of the dibutylbenzene resulting from experiment A, 10.0 g. of aluminum chloride and 342 g. of benzene was heated at reflux, approx. 85° for 5 hours. The reaction mixture was worked up as in experiment A. Fractionation yielded, after removal of benzene, 65.4 g. of material consisting of 53.6 g. of monobutylbenzene and 11.8 g. of dibutylbenzene and residue. This represents a 75 mole % conversion of the dibutylbenzene to monobutylbenzene.

The monobutylbenzene was shown from mass spectrometer analysis to be 99.2 mole % *n*-butylbenzene and 0.8% *s*-butylbenzene.

The residue from experiment A, on heating with aluminum chloride and excess benzene, did not yield any monobutylbenzene. It is therefore believed not to be a polybutylbenzene.

PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Steric Effects. III. Alkaline Saponification of Methyl 4-x-2,6-Dimethylbenzoates[1]

BY HARVEY L. GOERING,[2] THOR RUBIN AND MELVIN S. NEWMAN

RECEIVED AUGUST 14, 1953

The rates of saponification for a series of methyl 4-substituted-2,6-dimethylbenzoates in 60% dioxane–40% water solution in the 82–174° temperature range have been measured. These results indicate that the reactions proceed mainly by alkyl–oxygen fission. An interpretation of the effect of ortho-methyl groups on the rho values for ionization of para substituted benzoic acids in water–dioxane and water–alcohol solutions is advanced. The density of 60% dioxane–40% water solutions in the range 25–160° has been determined.

It has long been known that the alkaline hydrolysis of 2,6-disubstituted benzoates is extremely slow. This has been ascribed to steric hindrance.[3] We thought it of interest to study the effect of various groups in the 4-position in such cases and report here on the alkaline hydrolysis of methyl 4-x-2,6-dimethylbenzoates where x is hydrogen, methyl, bromine, nitro and amino.

The hydrolyses were conveniently measured at temperatures ranging from 82 to 114° (for x = NO_2) to 120–174° (for x = NH_2) in stainless steel tubes. It was originally thought that the rates measured would be those of the typical carbonyl addition reaction. However, from the magnitudes of the Arrhenius log *PZ* terms obtained and from the value of the Hammett rho factor we are led to believe that these alkaline hydrolyses took place mainly if not completely by an S_N2 type of displacement on the methyl carbon of the ester function. This type of ester cleavage has been observed previously in the reactions of methyl benzoate, mesitoate and 2,4,6-tribromobenzoate with methoxide ion[4] and in the alkaline hydrolysis of β-propiolactone.[5]

We attempted to verify this by O^{18} studies but owing to an error in procedure in two inportant cases involving benzoic esters which were used for checking purposes the results are not as clean cut as desired. Discussion of this phase will therefore be delayed until further experimental work is completed.

Experimental

Methyl 4-amino-2,6-dimethylbenzoate was prepared by reaction of diazomethane with 4-amino-2,6-dimethylbenzoic acid which was obtained essentially as described.[6] Because of the instability of the amino ester the hydrochloride was prepared. This compound crystallized in colorless needles (from aqueous methanol) which sublimed on heating.

Anal. Calcd. for $C_{10}H_{14}O_2NCl$: C, 55.7; H, 6.5; N, 6.5. Found[7]: C, 55.1, 55.1; H, 6.5, 6.5; N, 6.7, 6.5.

Methyl 4-bromo-2,6-dimethylbenzoate was prepared by esterification of 4-amino-2,6-dimethylbenzoic acid with diazomethane and diazotization of the ester in hydrobromic acid solution. The complex mercuric diazonium salt precipitated by mercuric bromide was mixed with sodium bromide and decomposed at 90–100° in a dry flask.[8] Methyl 4-bromo-2,6-dimethylbenzoate distilled at 107° at 3 mm. and crystallized from aqueous methanol in colorless crystals, m.p. 54°. The yield based on original amino acid was 24%.

Anal. Calcd. for $C_{10}H_{11}O_2Br$: C, 49.4; H, 4.6. Found: C, 49.0, 49.1; H, 4.3, 4.5.

4-Bromo-2,6-dimethylbenzoic acid was recovered as a product of the hydrolysis of its methyl ester. On recrystallization from benzene, the acid melted at 196.5–197.0°.[9]

Methyl 2,6-dimethyl-4-nitrobenzoate was prepared in 25% yield from 4-amino-2,6-dimethylbenzoic acid by esterification with diazomethane, diazotization in hydrochloric acid solution and treatment with sodium cobaltinitrite.[10] The ester distilled at 126–130° at 1 mm. and crystallized from aqueous methanol in pale yellow needles, m.p. 91.0–91.2°.

Anal. Calcd. for $C_{10}H_{11}O_4N$: C, 57.4; H, 5.3; N, 6.7. Found: C, 57.7, 57.6; H, 5.2, 5.3; N, 7.2, 7.0.

Methyl 2,6-dimethylbenzoate was prepared from 2,6-dimethylbenzoic acid by esterification with diazomethane.

---

[1] Taken from the Ph.D. thesis, O.S.U., 1950, of H. L. Goering.

[2] Standard Oil Company of Indiana Fellow, 1949–1950.

[3] V. Meyer, *Ber.*, **27**, 510 (1894); V. Meyer and J. J. Sudborough, *ibid.*, **27**, 3146 (1894).

[4] J. F. Bunnett, M. M. Robison and F. C. Pennington, THIS JOURNAL, **72**, 2378 (1950). The dissociation constant for mesitoic acid reported in this paper is that recorded in "Beilstein," Vol. IX, p. 553, which is in error. The correct value of 3.75 × 10^{-4} was reported by M. B. Breed, Bryn Mawr College Monograph, Vol. I, p. 1 (1901). The correlation between acid strength and cleavage by methoxide reported by B., R. and P. falls down if the correct value for the strength of mesitoic acid is used.

[5] See P. D. Bartlett and G. Small, Jr., THIS JOURNAL, **72**, 4867 (1950) and references therein.

[6] W. A. Noyes, *Am. Chem. J.*, **20**, 789 (1898). Improvements suggested by Dr. T. L. Jacobs, UCLA, were incorporated and these will be described by him.

[7] Analyses by Mrs. E. H. Klotz.

[8] von Swechten, *Ber.*, **65**, 1605 (1932); M. S. Newman and P. H. Wise, THIS JOURNAL, **63**, 2847 (1941).

[9] R. C. Fuson, S. L. Scott and R. V. Lindsey, Jr., *ibid.*, **63**, 1679 (1941), give m.p. 197–198°.

[10] H. H. Hodgson and E. Marsden, *J. Chem. Soc.*, **22** (1944).