n-amyl chloride. With 1.1 mole equivalent of aluminum chloride the yield of ethyl 4-*t*-butyl-5-bromo-2-furoate was 2%, and 91% of ethyl 5-bromo-2-furoate was recovered. The yield of alkylated bromo-ester was increased to 10% when 1.2 mole equivalent of aluminum chloride was used.

With 0.95 mole equivalent of aluminum chloride and *t*-butyl bromide, there was a quantitative recovery of ethyl 5-bromo-2-furoate.

Two check runs with 0.95 mole equivalent of aluminum chloride and isopropyl chloride gave no alkylated product and 95% of the initial bromo-ester was recovered. However, with 1.1 mole equivalent of aluminum chloride the yield of ethyl 4-isopropyl-5-bromo-2-furoate was 42%.

In an attempted alkylation of 0.084 mole of methyl *p*-methoxybenzoate, 0.084 mole of isopropyl chloride and 0.075 mole of aluminum chloride there was no evolution of hydrogen chloride and 94% of the initial ester was recovered. However, with 0.11 mole of aluminum chloride and 0.10 mole of isopropyl chloride there was obtained a 27% yield of isopropyl-4-methoxybenzoic acid[1a] and a 68% recovery of initial ester.

Solvents and Time of Reaction.—For purposes of comparison most of the reactions were allowed to continue for twenty-four hours. However, five hours was shown to be adequate for many of the alkylations. With *sym*-tetrachloroethane as a solvent, and a twenty-four hour reaction period, reaction between *n*-amyl chloride and ethyl 5-bromo-2-furoate gave a 21% yield of ethyl 4-*t*-butyl-5-bromo-2-furoate.

In an experiment using the same reagents, but carbon disulfide as a solvent and only a five-hour reaction period, the yield of alkylated bromo-ester was 16%.

With only one hour as the reaction period and carbon disulfide as the solvent, the yield of ethyl 4-*t*-butyl-5-bromo-2-furoate from reaction between *n*-octadecyl bromide and ethyl 5-bromo-2-furoate was 30%.

Of the several solvents examined, only carbon disulfide and *sym*-tetrachloroethane were effective. A careful search of products from several experiments involving ethyl 5-bromo-2-furoate and *n*-amyl chloride, with nitrobenzene as the solvent, revealed only a small quantity of *m*-dinitrobenzene, and this was probably a contaminant of nitrobenzene. When chlorobenzene was used, the ethyl 5-bromo-2-furoate was recovered, and a mixture of alkylated chlorobenzenes formed. There was no alkylation when kerosene was used as a medium, and no alkylation when no medium other than the reactants was used.

Hydrocarbon Fragments.—The evolved gases were collected and analyzed by customary procedures. With *n*-amyl chloride as the alkylating agent, the yields (based on the moles of alkyl halide) were 8.2% of isobutane and 5.7% of butane. The corresponding values when *n*-octadecyl bromide was used were 32% of isobutane and 7% of butane.

Summary

In the reaction of ethyl 5-bromo-2-furoate with butyl and higher alkyl halides, cleavage-rearrangement takes place in every case examined to give ethyl 4-*t*-butyl-5-bromo-2-furoate. Illustrative is the reaction with *n*-octadecyl bromide which gave a 46% yield of alkylated product.
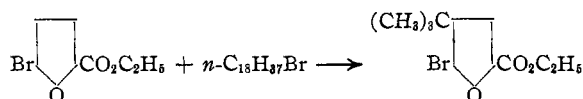
n-Amyl bromide gave in addition to ethyl 4-*t*-butyl-5-bromo-2-furoate, ethyl 5-*t*-butyl-2-furoate.

The effects of various factors like solvents, kind and concentration of catalysts, etc., were examined. It has been shown that the *alkylation* of some furan and benzene compounds requires more than one equivalent of aluminum chloride.

Some reaction mechanisms have been considered.

Friedel–Crafts Reactions: *n*-Octadecylbenzene, and Diacylations

BY HENRY GILMAN AND JOSEPH A. V. TURCK, JR.

Introduction

The unusual cleavage-rearrangement, described in the preceding paper,[1] of *n*-octadecyl bromide in its reaction with ethyl 5-bromo-2-furoate to give a 46% yield of ethyl 4-*t*-butyl-5-bromo-2-furoate suggested an examination of the octadecylbenzene prepared from *n*-octadecyl bromide and benzene.

We have found that the major product obtained by the alkylation of benzene is the *n*-octadecylbenzene. This was established by comparing the Friedel–Crafts product[2] with the product of the Wurtz–Fittig reaction[3] between *n*-octadecyl iodide and iodobenzene, and with the product obtained by the reduction of stearophenone[4] (*n*-heptadecyl phenyl ketone). The identity of the octadecylbenzenes obtained by these

(1) Gilman and Turck, THIS JOURNAL, **61**, 473 (1939).

(2) Seidel and Engelfried, *Ber.*, **69**, 2567 (1936).
(3) Krafft, *ibid.*, **19**, 2982 (1886).
(4) Adam, *Proc. Roy. Soc.*, (London), **A103**, 676 (1923).

three different procedures was established by the mixed melting points of the sulfonamides. If the method of mixed melting points is reliable with these compounds, then the octadecyl side chain must be normal for there is no reason for believing that rearrangement occurred in the Clemmensen reduction of the stearophenone.

In Friedel–Crafts reactions, polyalkylation is common, but polyacylation is unusual in a selected benzene nucleus. However, those benzene nuclei having groups like alkyl or hydroxyl which facilitate nuclear substitution do undergo diacylation. Some examples are the diacylation of *m*-xylene,[5] mesitylene,[6] 1,2,4,5- and 1,3,4,5-tetramethylbenzenes,[7] α-methoxynaphthalene,[8] phloroglucinol,[9] and the dibenzoate of hydroquinone.[10]

No diacylation was observed in a reaction between benzene and acetyl chloride.[6] It was considered more likely to find evidences of diacylation if the acylating compound was one of high molecular weight, for small quantities of a distearoylbenzene might be observed more readily than small quantities of a compound like diacetylbenzene.

No distearoylbenzene was isolated in forced reactions of stearophenone, stearoyl chloride and aluminum chloride. In one of these experiments carried out in nitrobenzene, the products other than initial stearophenone were stearone $[(C_{17}H_{35})_2C{=}O]$, and *o*- and *p*-chloroanilines. The *o*- and *p*-chloroanilines undoubtedly were formed as a consequence of a reduction–chlorination reaction on the nitrobenzene. A related reaction was reported recently with nitrobenzene

(5) Clar and John, *Ber.*, **62**, 3021 (1929).

(6) Meyer, *ibid.*, **29**, 1413 (1896).

(7) Baum and Meyer, *ibid.*, **28**, 3212 (1895).

(8) Popov, *J. Gen. Chem. (U. S. S. R.)*, **5**, 986 (1935); *C. A.*, **30**, 1049 (1936).

(9) Shinoda and Sato, *J. Pharm. Soc. Japan*, **51**, 576 (1931); *C. A.*, **26**, 1916 (1932).

(10) Doebner and Wolff, *Ber.*, **12**, 661 (1879).

and isopropyl chloride or isobutyl bromide.[11]

These experiments confirm the difficulty of diacylating benzene.[2,6] However, there is still the possibility that diacylation occurred and that prolonged heating may remove acyl groups.[7] Incidentally, the experiments add confirmation to the general knowledge that although lateral or side-chain rearrangement is sometimes observed with alkylbenzenes, it is exceptional with acylbenzenes.

Experimental Part

n-Octadecylbenzene.—A 50% yield of octadecylbenzene was obtained from the Friedel–Crafts reaction. The sulfonamide[2] melted at 99–100° after recrystallization from petroleum ether (b. p. 60–68°) and sublimation.

The Wurtz–Fittig reaction was carried out with 13.8 g. (0.036 mole) of *n*-octadecyl iodide, 8.2 g. (0.04 mole) of iodobenzene and 4.6 g. (0.2 g. atom) of sodium. The yield of octadecylbenzene was 35%, and the sulfonamide melted at 99–100°.

Stearophenone was reduced by the Martin[12] modification of the Clemmensen procedure. The yield was 24% and the sulfonamide melted at 99–100°. Mixed melting points of combinations of the three samples showed no depression.

Summary

There appears to be no significant rearrangement in the Friedel–Crafts alkylation of benzene by *n*-octadecyl bromide, a reaction which gives *n*-octadecylbenzene in 50% yield. The same product is obtained from a Wurtz–Fittig reaction between *n*-octadecyl iodide and iodobenzene, and from the Clemmensen reduction of stearophenone $(C_6H_5COC_{17}H_{35}$-*n*$)$.

There is no evidence of polyacylation or of lateral rearrangement in the reaction between stearophenone and stearoyl chloride.

(11) Gilman, Burtner, Calloway and Turck, THIS JOURNAL, **57**, 907 (1935).

(12) Martin, *ibid.*, **58**, 1438 (1936).