

The free energy of formation of sodium oxide corresponding to the mean of the mentioned heats of formation and the suggested entropy value is $\Delta F^\circ_{298.1} = -91,000$.

Summary

Specific heat data covering the temperature range 52.5 to 298.1°K. have been presented for sodium ortho-, meta-, and disilicates in the

anhydrous crystalline state. The corresponding entropies at 298.1°K. have been determined as 46.8 ± 0.6 , 27.2 ± 0.3 , and 39.4 ± 0.6 , respectively.

The value $S_{298.1} = 17$ is suggested as an approximation to the entropy of sodium oxide and $\Delta F^\circ_{298.1} = -91,000$ as an approximation to the free energy of formation.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

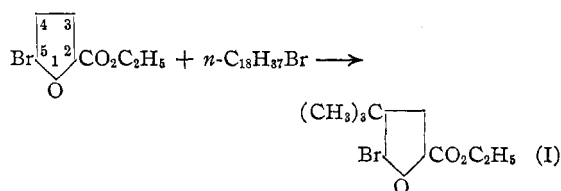
Orientation in the Furan Series. XI. Cleavage-Rearrangements in Friedel-Crafts Reactions

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

Introduction

In the Friedel-Crafts alkylation of methyl 2-furoate each of the four butyl chlorides, as well as butylene, gave some of the same product, namely, methyl 5-*t*-butyl-2-furoate.^{1a}

When higher alkyl halides^{1b} are used in the alkylation of ethyl 5-bromo-2-furoate, there is not only a rearrangement to the tertiary radical, but also a cleavage to a *t*-butyl radical, irrespective apparently of both the branching and length of the R group and of the nature of the X in the RX compound. One of the more striking reactions reported at this time is the 46% yield of ethyl 4-*t*-butyl-5-bromo-2-furoate from *n*-octadecyl bromide ($C_{18}H_{37}Br$).



t-Amyl alcohol alkylated after the fashion of the corresponding amyl halides, but no alkylation was observed with some olefins.

Replacement-Alkylation with *n*-Amyl Bromide.—When ethyl 5-bromo-2-furoate was first treated with *n*-amyl bromide the usual cleavage and rearrangement to a *t*-butyl radical took place; however, the *t*-butyl radical replaced the bromine and entered the 5-position to give ethyl 5-*t*-butyl-2-furoate in yields between 31 and 40%.

(1) (a) Gilman and Calloway, *THIS JOURNAL*, **55**, 4197 (1933); (b) Gilman and Burtner, *ibid.*, **57**, 909 (1935); (c) Gilman, Burtner, Calloway and Turck, *ibid.*, **57**, 907 (1935); (d) Gilman, Calloway and Burtner, *ibid.*, **57**, 906 (1935).

This highly unusual result, when it is considered that a reaction like (I) took place with very closely related halides, prompted experiments in which some factors were varied.² It was subsequently found possible, in separate experiments, to obtain not only a mixture of ethyl 5-*t*-butyl-2-furoate and ethyl 4-*t*-butyl-5-bromo-2-furoate, but also the latter compound exclusively.

A replacement-substitution reaction has been noted in an acylation. Nitrofuran, propionyl chloride and titanium chloride give 5-chlorofuryl ethyl ketone.^{1c}

Alkylation with Other Furan Derivatives. A. Ethyl 5-Chloro-2-furoate.—It seemed reasonable to attribute the cleavage-rearrangement reaction to a mechanism concerned in part with steric hindrance. Accordingly, ethyl 5-chloro-2-furoate was brought into reaction with *n*-amyl chloride in order to determine whether the smaller nuclear chlorine might permit the introduction of an amyl radical. However, the usual cleavage-rearrangement took place, and a *t*-butyl radical was substituted in the 4-position to give ethyl 4-*t*-butyl-5-chloro-2-furoate. A more significant test of the steric factor would be the alkylation of the as yet unknown ethyl 5-fluoro-2-furoate.

B. Ethyl 4-Bromo-2-furoate.—This bromo ester was selected in order to establish whether a cleavage would take place when an α -position in furan is available. It is known that there is apparently no cleavage when methyl 2-furoate is alkylated by *n*-amyl chloride and *n*-hexyl bromide, for the products isolated were methyl 5-

(2) See Experimental Part.

amyl-2-furoate and methyl 5-hexyl-2-furoate, respectively. However, when ethyl 4-bromo-2-furoate was treated with *n*-amyl chloride there was a cleavage, despite the availability of an α -position, and the product isolated was ethyl 5-*t*-butyl-2-furoate. The bromine atom must have been removed after alkylation rather than before inasmuch as ethyl 2-furoate alkylates without cleavage.

C. Ethyl 4,5-Dibromo-2-furoate.—In this ester both the 4- and the 5-positions are blocked, and the remaining 3-position is very resistant to substitution as evidenced by its quantitative recovery in an attempted nitration.³ It might have been expected from the results already described that a bromine would be replaced in a cleavage-alkylation if a halide higher than C_4H_9X were used. Actually, there was no reaction with *n*-amyl chloride.

Likewise, since *n*-amyl bromide was observed to displace the bromine in ethyl 5-bromo-2-furoate by a *t*-butyl group, it seemed possible that a related reaction would take place with ethyl 4,5-dibromo-2-furoate. However, there was no reaction and the furan compound was recovered quantitatively.

D. 5-Bromo-2-furfural.—2-Furfural has been alkylated by isopropyl chloride to give 4-isopropyl-2-furfural,^{1d} the first unequivocal evidence of a β -substitution reaction of furan when one α -position is available. By analogy, therefore, with the alkylation of 2-furfural and of ethyl 5-bromo-2-furoate one might have expected reaction with *n*-amyl chloride to introduce a *t*-butyl group into the 4-position. However, no alkylation product was isolated and most of the 5-bromo-2-furfural was recovered.

Effect of Ferric Chloride.—Ferric chloride in varying quantities in aluminum chloride is known to affect some Friedel-Crafts reactions,⁴ particularly acylations.

Aluminum chloride containing quantities of ferric chloride varying between 0.002 to 0.1% gave the same alkylation product in reactions between ethyl 5-bromo-2-furoate and *n*-amyl chloride, although the yields were slightly higher with aluminum chloride which was relatively free of iron.

(3) Studies by George F. Wright.

(4) Some recent references are: Boswell and McLaughlin, *Can. J. Research*, **1**, 400 (1929); Gallay and Whitby, *ibid.*, **2**, 31 (1930); Riddell and Noller, *THIS JOURNAL*, **54**, 290 (1932); Wertyporoch, Kowalski and Roeske, *Ber.*, **66**, 1232 (1933); Martin, Pizzolato and McWaters, *THIS JOURNAL*, **57**, 2584 (1935). See, also, Calloway, *Chem. Rev.*, **17**, 327 (1935).

The ferric chloride appeared to have a distinct effect upon the course of the unusual bromine-replacement reaction observed with *n*-amyl bromide. When aluminum chloride containing a very small quantity of ferric chloride was used, none of the bromine-replacement reaction was noted, and ethyl 4-*t*-butyl-5-bromo-2-furoate was formed. The addition of ferric chloride to this aluminum chloride in quantity to bring the iron to 0.12%, was sufficient to effect the bromine-replacement reaction to a small extent. Of greater significance were experiments in which one of the commercial samples of aluminum chloride that produced bromine-replacement was resublimed just prior to use. Purification in this manner gave an aluminum chloride which induced no bromine-replacement reaction. Unfortunately, ferric chloride alone was not sufficiently reactive to effect any reaction under the experimental conditions used.

Concentration of Aluminum Chloride.—Generally, alkylations by the Friedel-Crafts reaction can be accomplished by less than one mole equivalent of aluminum chloride, whereas acylations require at least one mole equivalent of "catalyst." Although the reactions described in this paper are alkylations, it was found that at least one equivalent of aluminum chloride was required. No alkylation took place with 0.95 mole equivalent, and 1.1 equivalents were sufficient to induce alkylation. The extra quantity of aluminum chloride required in the alkylations of the halogenofuroates is not due to the cleavage reaction, for methyl *p*-methoxybenzoate which was alkylated without cleavage required an amount of aluminum chloride in excess of one equivalent. It is quite probable that the first equivalent of aluminum chloride is tied up by a complex or coördinate compound with the carboalkoxy group.

Mechanism of Reaction.—The invariable introduction of a radical having four carbon atoms suggests that the *t*-butyl group so introduced comes from the four carbon atoms of the furan nucleus. This has some plausibility because the nucleus of simple furan compounds is readily cleaved by acids. However, negatively substituted furans, like ethyl 5-bromo-2-furoate, are quite resistant to the action of acids. It is true that a more stable nucleus such as benzene can undergo destructive alkylation to give ethylbenzene.⁵ But in this case the low yield of ethyl-

(5) Ipatieff and Komarewsky, *THIS JOURNAL*, **56**, 1926 (1934).

benzene (1.7%) was obtained under relatively drastic conditions: heating benzene at 125° in the presence of aluminum chloride and hydrogen chloride.

An analysis of various experiments shows that no significant quantity of the *t*-butyl radicals came from the furan ring itself. First, blank runs under conditions of alkylation, with the exception of the omission of alkyl halide, resulted in almost complete recovery of the initial ester or the corresponding acid. In some of these experiments, hydrogen halide was bubbled into the mixture in order to simulate more closely the Friedel-Crafts conditions. Second, numerous experiments gave no evidence of alkylation. Some of these are the attempted alkylations with olefins, and moderate heating (50–80°) in the absence of any solvent. Third, in the alkylation by *n*-octadecyl bromide the yield of alkylated product was 46% and the yield of recovered initial ester was 45%. In this, as well as in some other experiments, most of the furan nucleus is accounted for as such after significant alkylation has taken place.

The *t*-butyl group must then come from the alkyl halide. Cleavage to the *t*-butyl group can either precede (or be simultaneous with) or follow alkylation. It is quite unlikely that cleavage follows alkylation, even though it is possible to alkylate other furan compounds, like methyl 2-furoate and furfural, without cleavage. An answer must wait on the synthesis and then attempted cleavage by aluminum chloride of a compound like ethyl 4-*n*-amyl-5-bromo-2-furoate. It is pertinent to observe that in the benzene series cleavage of alkylated benzenes occurs at the carbon-carbon bond between the ring and the side-chain.⁶

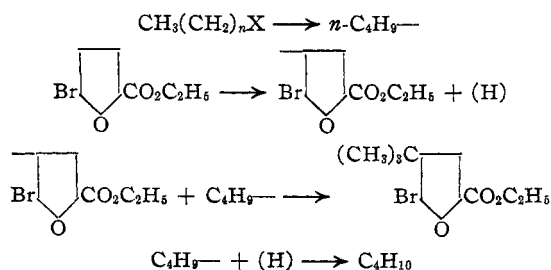
What may happen is that the alkyl halide, or some compound derived from it, is cleaved into fragments small enough to be introduced into the sterically hindered β -position. An examination of cleavage products from the reaction between ethyl 5-bromo-2-furoate and *n*-amyl chloride showed that *n*-butane and isobutane were the chief fragments, relatively small quantities of fragments having less than four carbon atoms being evolved. There was no evidence of any small molecular weight alkyl chloride, like methyl chloride or ethyl chloride. The copious evolution of hydrogen chloride suggests the intermediate

formation of an olefin as the active alkylating agent. Olefins would help account for the formation of the highly branched tertiary radical. However, unless the olefins were in an activated state it is difficult to see how they were the precursors of alkylation when one considers the numerous negative results with olefins like butylene (see Experimental Part).

With only *n*-amyl chloride and aluminum chloride (and no solvent) there was a prompt evolution of hydrogen chloride, butanes and pentanes. Here the non-volatile product was of a resinous nature and unsaturated, judging from its practically complete solubility in concd. sulfuric acid. The absence, under our experimental conditions, of any gaseous products having less than four carbon atoms is noteworthy, since it indicates that the decomposition of alkyl halides, when treated with aluminum chloride, proceeds by a different course when carried out in a solvent containing ethyl 5-bromo-2-furoate.

The fragments from a reaction between ethyl 5-bromo-2-furoate, *n*-octadecyl bromide and aluminum chloride in *sym*-tetrachloroethane consisted of butanes, pentanes, and hexanes, together with some higher liquid fractions which were difficult to separate cleanly.

Paraffins are known to be cleaved predominantly by the action of aluminum chloride and hydrogen chloride to *n*-butane and isobutane.⁶ The exact mechanism is not yet understood. If the alkyl halides cleave under the conditions of the furan experiments to give units of four carbon atoms, it is possible that free radicals may be the active precursors in chain reactions. These free radicals may combine, in part, with the loosened or detached nuclear hydrogen to account for the butanes isolated; and also combine with the free radical (or its equivalent) resulting from the bromofuroate to give the alkylated bromofuroate. A rough schematic presentation which omits the intermediary function of the aluminum chloride complexes would be the following



(6) Egloff, Wilson, Hulla and Van Arsdell, *Chem. Rev.*, **20**, 345 (1937).

Reports have appeared recently of somewhat related reactions in the benzene series. Grosse and Ipatieff⁷ obtained isobutane, *t*-butylbenzene and di-*p*-*t*-butylbenzene from the reaction of 2,2,4-trimethylpentane with benzene. Also, Ipatieff and Pines⁸ obtained mono-, di- and probably tri-*t*-butylbenzenes from diisobutylene and benzene. Smith and Rodden^{9a} obtained a high yield of *p*-*t*-butylphenol from phenol and diisobutylene, and the same product from inter-action of *p*-*t*-octylphenol and phenol.

Some general differences between the cleavage-rearrangements in the furan and benzene series are: (1) the predominant and in many cases exclusive introduction of the *t*-butyl group irrespective of the kind of alkyl halide having four or more carbons; (2) the mild conditions of room temperature with carbon disulfide as a medium; and (3) an aromatic nucleus having two negatively substituted groups (bromine and carbo-alkoxy). It remains to be determined whether related benzene types will show the same kind of cleavage-rearrangement. From earlier work^{1b} it is known that there are some essential differences in the direction of the Friedel-Crafts reaction in the furan and the benzene series. One illustration is the formation of *m*-alkylated products when benzaldehyde is treated with isopropyl chloride and *t*-butyl chloride; whereas furfural with isopropyl chloride undergoes alkylation in the 4-position, but with *t*-butyl chloride alkylation takes place in the 5-position.

Experimental Part

Alkylation of Ethyl 5-Bromo-2-furoate with Alkyl Halides.—Details of a typical alkylation follow, and the general results are contained in Table I. The quantities of reagents used were 21.9 g. (0.1 mole) of ethyl 5-bromo-2-furoate, 10.6 g. (0.1 mole) of *n*-amyl chloride, 26.7 g. (0.2 mole) of aluminum chloride and 200 cc. of carbon disulfide. Reaction was carried out in a 500-cc. three-necked flask provided with a stirrer, dropping funnel, and efficient condenser fitted with a drying tube containing calcium chloride.

The order of addition of the reagents appeared to be without effect; however, the alkyl halide generally was added in about 50 cc. of the carbon disulfide, over a fifteen-minute period, to the other reactants. Stirring was continued for twenty-four hours, at the end of which time the contents were poured slowly (and with vigorous stirring) into a 1:1 mixture of cracked ice and water. The mixture

was shaken in a separatory funnel and the lower carbon disulfide layer drawn off. Considerable insoluble solid material was usually present, and this proved to be 5-bromo-2-furoic acid. The acid was brought into solution by ether, after which three extractions with about 50 cc. of a saturated sodium bicarbonate solution sufficed to remove the acids completely.

The neutral solution was dried, the mixed solvents distilled off, and the residual liquid fractionated under reduced pressure. In all cases, at least two fractionations were carried out. The higher fractions, b. p., 142–180° (5 mm.), gave no definite cuts, and turned to semi-solid, black tars. Because they did not saponify, they were generally considered to be polymerization products of the fragments formed from cleavage alkylation. In addition, there usually remained in the distilling flask about 2 to 7 g. of tarry residue which solidified on cooling, but which could not be saponified.

All of the distillates contained traces of sulfur compounds which appeared to be responsible for the dark red color, particularly of the higher boiling fractions. Dithio esters are products of some other Friedel-Crafts reactions carried out in carbon disulfide.^{1a} These impurities resisted removal by fractional distillation and added to the difficulties in purifying and identifying the products. The disagreeable odor of the several fractions was also due to these sulfur compounds. Their nuisance value was compensated for by their value in diagnosing reaction: in general, where no alkylation took place in carbon disulfide, no sulfur compounds were formed and consequently there was no red coloration.

The first fraction, 86–91° (5 mm.), was practically pure, recovered ethyl 5-bromo-2-furoate; the second fraction, 91–130° (5 mm.), was a mixture of ethyl 5-bromo-2-furoate and ethyl 4-*t*-butyl-5-bromo-2-furoate, with the latter predominating and the third fraction, 130–142° (5 mm.), was ethyl 4-*t*-butyl-5-bromo-2-furoate. The wide boiling range of the product of alkylation was due to small amounts of resinous material and the sulfur compounds. Further distillation did not give much purer products, so that two fractionations generally constituted the extent of purification of the esters.

Additional purification, and identification, was carried out with the acids obtained by hydrolyzing the esters by refluxing for ten minutes with 20% alcoholic potassium hydroxide. After cooling, the alcoholic solution was added to several times its volume of water, whereupon the red color disappeared. The filtered solution was acidified by hydrochloric acid using congo red as the indicator. The acids from the higher boiling fractions of esters either gave a crystalline deposit gradually on standing, or a brown oil which crystallized slowly on standing in the cold.

Final purification of the mixture of acids was effected by either fractional sublimation alone or in combination with fractional recrystallization. The alkylated acid is more soluble in water and organic solvents than is the non-alkylated acid. Identification was completed by the method of mixed melting points. The yields of alkylated acid given in Table I are based on the theoretically possible amounts, and these yields when added to the yields of recovered 5-bromo-2-furoic acid account for practically all of the initial furoic ester.

(7) Grosse and Ipatieff, *THIS JOURNAL*, **57**, 2415 (1935).

(8) Ipatieff and Pines, *ibid.*, **58**, 1056 (1936).

(9) (a) Smith and Rodden, *ibid.*, **59**, 2353 (1937). See also Tilicheev and Kuruindin, *Neflyanoe Khim.*, **19**, 586 (1930) [*C. A.*, **25**, 3469 (1931)]; (b) Smith, *THIS JOURNAL*, **59**, 899 (1937).

TABLE I

YIELDS OF ETHYL 4- <i>t</i> -BUTYL-5-BROMO-2-FUROATE			
Alkyl halide	% yield	Alkyl halide	% yield
<i>n</i> -C ₄ H ₉ Cl	26	<i>n</i> -C ₆ H ₁₃ Cl	20
<i>t</i> -C ₄ H ₉ Br	15	<i>n</i> -C ₆ H ₁₃ Br	6
<i>n</i> -C ₆ H ₁₁ Cl	15	<i>n</i> -C ₁₂ H ₂₅ Br	13
<i>t</i> -C ₆ H ₁₁ Cl	6	<i>n</i> -C ₁₆ H ₃₃ Br	20
<i>i</i> -C ₆ H ₁₁ Br	20	<i>n</i> -C ₁₈ H ₃₇ Br	46
<i>n</i> -C ₈ H ₁₇ I	25		

Some of the experiments, the results of which are given in Table I, were checked and re-checked. In addition, the reaction with *n*-octadecyl bromide was checked by Miles R. McCorkle using independent materials. During the reaction with *n*-amyl iodide, which was allowed to continue for only six hours, iodine was liberated.

An alicyclic halide (cyclohexyl chloride) and an aryl-alkyl halide (γ -phenyl-*n*-propyl bromide) did not give any of the ethyl 4-*t*-butyl-5-bromo-2-furoate.

From a reaction between methyl 5-bromo-2-furoate and *n*-amyl chloride, the yield of methyl 4-*t*-butyl-5-bromo-2-furoate was 22%.

Alkylation with *t*-Amyl Alcohol.—Alkylation of ethyl 5-bromo-2-furoate in carbon disulfide with *t*-amyl alcohol gave a 10% yield of 4-*t*-butyl-5-bromo-2-furoic acid, subsequent to saponification.

Unsuccessful Alkylations with Olefins.—None of the ethyl 4-*t*-butyl-5-bromo-2-furoate was isolated in attempted alkylations with butylene, diisobutylene, β -*n*-amylene and cyclohexene. The negative results with the open-chained alkenes were unexpected in view of the successful alkylation^{1a} of methyl 2-furoate by butylene and the general applicability of olefins as alkylating agents.

Reaction with *n*-Amyl Bromide.—In two reactions with ethyl 5-bromo-2-furoate, the yields of 5-*t*-butyl-2-furoic acid were 31 and 40%. This product was always isolated as the acid, the ester being hydrolyzed readily. That is, the acid solution resulting from the decomposition of the aluminum chloride complex with water seemed to be sufficient to hydrolyze completely the ethyl 5-*t*-butyl-2-furoate. Because of the anomalous results with *n*-amyl bromide this halide was characterized not only by the usual physical constants, but also by a derivative.¹⁰ The *n*-amylmagnesium bromide obtained from it was treated with α -naphthyl isocyanate to give *n*-capro- α -naphthalide (m. p. 93–95°) which was shown to be identical with a sample prepared from *n*-caproyl chloride and α -naphthylamine.

The alkylation reaction also was checked by J. M. Straley using independent materials.

That grade of aluminum chloride which with *n*-amyl bromide gave a mixture of ethyl 4-*t*-butyl-5-bromo-2-furoate and ethyl 5-*t*-butyl-2-furoate, yielded the same results when the particle sizes were coarse, medium, and fine.

Reaction with *t*-Amylbenzene.—It has long been known that aluminum chloride makes possible the migration of an alkyl group from one aromatic compound to another. A recent illustration^{9b} is the reaction between *p*-*t*-amylphenol and benzene to give phenol and *t*-amylbenzene.

An unidentified acid was obtained in small quantities

from the reaction of *t*-amylbenzene with ethyl 5-bromo-2-furoate. The acid melted at 187–187.5° after recrystallization from aqueous methanol, was free of halogen, had a neutralization equivalent of 185.2 (and 184.5), and the molecular formula calculated from the carbon and hydrogen analyses was C₁₁H₁₆O₂. The presence of only two oxygen atoms showed the compound not to be a furoic acid.

Alkylation of Ethyl 4-Bromo-2-furoate.—This bromo ester was prepared in essential accordance with the directions of Hill and Sanger.¹¹ Alkylation was effected by *n*-amyl chloride under the general conditions used in alkylations of ethyl 5-bromo-2-furoate. In addition to 5-*t*-butyl-2-furoic acid (identified by the method of mixed melting points) there were obtained two crude acids melting, respectively, over the ranges 112.5–130° and 110–130°.

Alkylation of Ethyl 5-Chloro-2-furoate.—The new acid obtained by alkylation with *n*-amyl chloride under the general conditions melted at 172–173° after recrystallization from petroleum ether (b. p. 75–115°).

Anal. Calcd. for C₉H₁₁O₃Cl: Cl, 17.50; neut. equiv., 202.6. Found: Cl, 17.58 and 17.76; neut. equiv., 201.6 and 202.5.

The same acid (mixed melting point) was obtained when *t*-butyl bromide was used as the alkylating agent.

Ethyl 4,5-Dibromo-2-furoate.—The alkyl halides tried in the attempted alkylation of ethyl 4,5-dibromo-2-furoate were: *n*-amyl chloride, *n*-amyl bromide, *t*-butyl bromide and isopropyl chloride. Inasmuch as isopropyl chloride showed no evidence of reaction under the usual conditions at room temperature, the mixture was refluxed (46°) for six hours and then stirred at room temperature for an additional eighteen hours.

In each experiment the recovery of ethyl 4,5-dibromo-2-furoate was practically quantitative.

Effect of Catalysts.—The yields of alkylation products given in Table I were obtained with an aluminum chloride purchased from Baker and Adamson, "Lot No. 6," and containing a maximum of 0.08% of iron as the main impurity.

When *n*-amyl bromide was again used as the alkylating agent with Eastman resublimed aluminum chloride (containing a maximum of 0.02% of iron) 4-*t*-butyl-5-bromo-2-furoic acid but no 5-*t*-butyl-2-furoic acid was isolated. This experiment was checked. The addition of a drop of water to the aluminum chloride did not affect the course of reaction.

The addition of anhydrous ferric chloride to Eastman resublimed aluminum chloride in sufficient quantity to bring the iron content up to 0.12% gave, in an *n*-amyl bromide alkylation, both 4-*t*-butyl-5-bromo-2-furoic acid and 5-*t*-butyl-2-furoic acid.

The experiments on particle size were carried out with aluminum chloride kindly supplied by the Hooker Electrochemical Co., through the kindness of Dr. Marsh.

In the experiments concerned with the effect of concentration of aluminum chloride, the aluminum chloride was added by means of a hopper to the carbon disulfide solution of the alkyl halide and the compound to be alkylated. Using 0.95 mole equivalent of aluminum chloride, no alkylated product was recovered in an experiment with

(10) Gilman and Furry, *THIS JOURNAL*, **50**, 1214 (1928).

(11) Hill and Sanger, *Proc. Am. Acad. Arts Sci.*, **21**, 135 (1885).

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%.

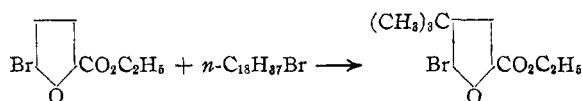
Of the several solvents examined, only carbon disulfide and *sym*-tetrachloroethane were effective. A careful search of products from several experiments involving ethyl 5-bromo-2-furoate and *n*-amyl chloride, with nitrobenzene as the solvent, revealed only a small quantity of

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.

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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 ob-

tained by the alkylation of benzene is the *n*-octadecylbenzene. This was established by comparing the Friedel-Crafts product² with the product of the Wurtz-Fittig reaction³ between *n*-octadecyl iodide and iodobenzene, and with the product obtained by the reduction of stearophenone⁴ (*n*-heptadecyl phenyl ketone). The identity of the octadecylbenzenes obtained by these

(2) Seidel and Engelfried, *Ber.*, **69**, 2567 (1936).

(3) Kraft, *ibid.*, **19**, 2982 (1886).

(4) Adam, *Proc. Roy. Soc.*, (London), **A103**, 676 (1923).

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