

### Summary

1. Under the conditions used by us sodium ethylate is not a useful reagent for obtaining the sodium salt of phenylacetonitrile.
2. A considerable quantity of sodium phenylacetonitrile is undoubtedly formed in the reaction of the nitrile with sodium ethylate but much of the salt condenses with the mononitrile to form a dinitrile.
3.  $\alpha$ -Phenylbutyronitrile was not found to condense with itself under the influence of sodium ethylate in ether.
4. The syntheses of the chloride and amide of  $\alpha$ -phenylbutyric acid are reported.

CHICAGO, ILLINOIS

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

## CARBON TETRABROMIDE AS A BROMINATING AGENT<sup>1</sup>

BY W. H. HUNTER AND D. E. EDGAR

RECEIVED JANUARY 2, 1932

PUBLISHED MAY 7, 1932

During the study of certain reactions of carbon tetrabromide and aniline in xylene solution, it was observed that the xylene was brominated. Accordingly, an investigation was started with the point of view of determining the possible use of carbon tetrabromide as a brominating agent. In the case of the majority of compounds studied, bromination with this reagent took place, and when this occurred bromoform was always a by-product. Most of the bromo compounds prepared in this work can be made more easily by other methods, so that, as a rule, the use of carbon tetrabromide does not have any advantages over the commoner methods, but our experiments indicate that there are certain regularities with brominations using carbon tetrabromide that may be very useful, and the most important of these is the preferential side chain bromination of alkylbenzenes.

### Experimental Part

**Preparation of Carbon Tetrabromide.**—The method of Wallach<sup>2</sup> served as a basis for our modified preparation of carbon tetrabromide from acetone and sodium hypobromite. The preparation as described is suitable for the production of large quantities of carbon tetrabromide in good yield. Since bromoform is a by-product in all cases of brominations described here, use was also made of a method similar to Habermann's,<sup>3</sup> involving bromoform and aqueous sodium hypobromite. Although Habermann stated that direct light was necessary, it was found that as good a yield of carbon tetrabromide could be obtained in the complete absence of light.

<sup>1</sup> The work described in this paper constituted part of a thesis submitted to the graduate faculty of the University of Minnesota by Donald E. Edgar in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1927. This paper was prepared by the junior author after the death of Dr. Hunter.—[L. I. SMITH.]

<sup>2</sup> Wallach, *Ann.*, **275**, 149 (1893).

<sup>3</sup> Habermann, *ibid.*, **167**, 174 (1873).

(a) **From Acetone.**—A four-liter container (fitted with a mechanical agitator) was approximately half-filled with shaved ice. To this was added 2500 cc. of sodium hydroxide solution containing 150 g. of sodium hydroxide to the liter; 200 cc. of bromine was added rapidly with stirring. Then 60 cc. of acetone was added in small portions (5–10 cc.), time being allowed after each addition for the milky precipitate formed (probably bromoform) to be converted into lumps of carbon tetrabromide. After addition of this amount of acetone, 1-cc. portions were added cautiously until the characteristic yellow hypobromite color had been discharged. The crude carbon tetrabromide was separated by filtration and purified by crystallization from alcohol.

(b) **From Bromoform.**—A sodium hypobromite solution was prepared as in (a) but with only one-fourth of the amounts of materials. This is sufficient to convert 150 g. of bromoform to carbon tetrabromide. All of the bromoform was added at one time and the mixture was shaken or stirred vigorously.

**Procedure in Bromination Experiments.**—The reactions were carried out by heating carbon tetrabromide with various materials in sealed tubes, in the proportions of 1:1 unless otherwise noted. The temperature, in general, was 150–180°, and the time of heating about eight hours. In practically all cases, separation and purification of resulting products was accomplished by fractional distillation under diminished pressure. Identification of the products was by analysis for bromine, together with physical properties. The method of analysis was that of Stepanoff, as modified by Drogin and Rosanoff,<sup>4</sup> which was found to be rapid and convenient.

TABLE I  
RESULTS OF EXPERIMENTS IN WHICH ALIPHATIC COMPOUNDS WERE THE REACTANTS  
WITH CARBON TETRABROMIDE

Reactants with CBr <sub>4</sub>	Product	Yield, %
<i>n</i> -Heptane	Decomposition	..
Acetic acid	Bromoacetic acid	32.4
Propionic acid	$\alpha$ - and $\beta$ -monobromopropionic acids (mixture)	42.2
<i>Sym</i> .-tetrabromoethane	Pentabromoethane	10.1
	Hexabromoethane	2
Pentabromoethane	Hexabromoethane	Trace

TABLE II  
RESULTS WITH AROMATIC COMPOUNDS

Reactants with CBr <sub>4</sub>	Product	Yield, %
Benzene	Bromobenzene	67.6
Toluene	Benzyl bromide	76.9
Ethylbenzene	1-Phenyl-1-bromoethane	66.6
Ethylbenzene <sup>a</sup>	1-Phenyl-1,2-dibromoethane	70.3
<i>n</i> -Propylbenzene	1-Phenyl-1-bromopropane	46.7
Cumene	Decomposition	..
<i>m</i> -Xylene	<i>m</i> -Xylyl monobromide	67.3
<i>m</i> -Xylene <sup>a</sup>	<i>m</i> -Xylylene dibromide	48.4
Durene	Duryl monobromide	33.5
Durene <sup>b</sup>	Addition product, 1:1	100
Naphthalene	$\alpha$ -Bromonaphthalene	74.5

<sup>a</sup> Two moles of carbon tetrabromide to one of reactant. <sup>b</sup> Room temperature in carbon disulfide solution.

<sup>4</sup> Drogin and Rosanoff, *THIS JOURNAL*, **38**, 711 (1916).

In the study of aromatic hydrocarbons, described above in Table II, several interesting facts were noted. Bromination, by this method, takes place preferentially in the side chain rather than in the ring: the first point of attack being, in these cases, the alpha carbon of the chain. The decomposition of isopropylbenzene, whereas *n*-propylbenzene is brominated, suggests a method of differentiating between normal and iso linkages to the ring.

**Duryl Monobromide** ( $C_{10}H_{13}Br$ ).—This compound, which has not heretofore been prepared, resulted from the reaction of carbon tetrabromide and durene in the general manner described above and in Table II. Duryl monobromide is a clear, practically colorless liquid boiling at 110–112° under a pressure of 4 mm. It has a not unpleasant odor, somewhat resembling that of benzyl bromide, but is free from lachrymatory action. With alcoholic silver nitrate it gives an immediate precipitate of silver chloride, while monobromodurene, a solid having a melting point of 61°—the only other monobromo derivative of durene—gives no precipitate.

*Anal.* Calcd. for  $C_{10}H_{13}Br$ : Br, 37.51. Found: (Stepanoff) Br, 37.78, 37.69; (Carius) Br, 37.88, 37.82; (alc.  $AgNO_3$ ) Br, 37.81, 37.86.

**Durene—Carbon Tetrabromide Addition Product** ( $C_{10}H_{14} \cdot CBr_4$ ).<sup>5</sup>—Durene and carbon tetrabromide were dissolved in equivalent molecular proportions in an excess of carbon disulfide. The solution was allowed to stand at room temperature until the carbon disulfide had evaporated. The material remaining was in the form of large, well-defined crystals different in form from those of durene or of carbon tetrabromide, m. p. 84–86°. Mixed melting points of this material with either durene or carbon tetrabromide gave a lowering of the melting point.

*Anal.* Calcd. for  $C_{10}H_{14} \cdot CBr_4$ : Br, 68.62. Found: Br, 68.29, 68.51.

TABLE III  
REACTIONS WITH AROMATIC COMPOUNDS

Reactants with $CBr_4$	Product	Yield, %
Bromobenzene	<i>p</i> -Dibromobenzene	42.5
<i>p</i> -Dibromobenzene	No reaction	..
Benzyl bromide	Benzal bromide	55.3
	Benzal bromide	74.5 <sup>d</sup>
Benzyl bromide <sup>a</sup>	Benzotribromide	21.4
Benzal bromide	Benzotribromide	27.2
Phenol <sup>b</sup>	(Aurin)	..
Aniline <sup>c</sup>	(Pararosaniline)	..

Nitrobenzene, *m*-dinitro benzene, and benzoic acid gave no reaction, even on prolonged heating, while hydroquinone was completely decomposed.

<sup>a</sup> Two moles of carbon tetrabromide to one of reactant. <sup>b</sup> One mole of carbon tetrabromide to ten of reactant; refluxed for thirty minutes. <sup>c</sup> One mole of carbon tetrabromide to thirteen of reactant; refluxed for one hour. <sup>d</sup> Temperature, 210°.

Table III records the reactions of various aromatic compounds. It is interesting to note that bromination did not take place with any of the compounds having a meta orienting group already present. Phenol and carbon tetrabromide when heated together at atmospheric pressure gave a bright red material which was not studied further at this time. It was perhaps aurin, since Gomberg and Snow<sup>6</sup> have described the formation of this dye from phenol and carbon tetrachloride. Likewise, in the case of aniline, para-

<sup>5</sup> We wish to express our thanks to Dr. L. I. Smith for his generosity in providing the durene and bromodurene which made possible these experiments.

<sup>6</sup> Gomberg and Snow, *THIS JOURNAL*, **47**, 198 (1925).

rosaniline was perhaps the product since Hofmann<sup>7</sup> obtained it similarly by the action of carbon tetrachloride.

It will be noted in Table III that benzotribromide was the product of two reactions. This compound is described here for the first time, as far as the writers are aware. A search of the literature revealed only one mention<sup>8</sup> of this compound and that was in a statement to the effect that benzotrichloride (or bromide) is readily hydrolyzed by water or potassium hydroxide to benzoic acid. It was found that several hours of heating with 10% sodium hydroxide was required to bring about hydrolysis of a 3-g. sample.

**Benzotribromide** ( $C_7H_5Br_3$ ).—Benzotribromide resulted from the reaction of two equivalents of carbon tetrabromide with one of benzyl bromide and also from one equivalent of carbon tetrabromide with one of benzal bromide. Hydrolysis of the product resulted in the formation of benzoic acid.

Benzotribromide is a colorless crystalline material, very soluble in alcohol or ether, less soluble in petroleum ether, insoluble in water: m. p. 56–57°.

*Anal.* Calcd.: Br, 72.91. Found: Br, 72.76, 72.61 (Stepanoff); 72.85 (alc.  $AgNO_3$ ).

### Summary

1. Carbon tetrabromide will react with various organic materials through the exchange of a bromine atom for a hydrogen. Bromoform is always the by-product of such bromination.

2. Carbon tetrabromide brominates selectively the side chains of the benzene hydrocarbons instead of attacking the ring.

3. Duryl monobromide, benzotribromide, and an addition product of durene and carbon tetrabromide are described.

<sup>7</sup> Hofmann, *J. prakt. Chem.*, **77**, 191 (1859); **87**, 226 (1862).

<sup>8</sup> Fry, *THIS JOURNAL*, **36**, 1043 (1914).

MINNEAPOLIS, MINNESOTA

---

[CONTRIBUTION FROM THE WALKER CHEMICAL LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

## SUBSTITUTED PHENYLACETONITRILES AND DERIVATIVES. 1-PHENYL-1-CYANOCYCLOPROPANE, ALPHA-PHENYL- GAMMA-HYDROXYBUTYRONITRILE, ALPHA-PHENYL-GAMMA- CHLOROBUTYRONITRILE AND ALPHA- PHENYLCROTONONITRILE<sup>1</sup>

BY EDWIN C. KNOWLES AND JOHN B. CLOKE

RECEIVED JANUARY 2, 1932

PUBLISHED MAY 7, 1932

In the development of a series of investigations on sundry cyclic ketimines, imino esters and heterocyclic nitrogen compounds, supplies of  $\alpha$ -alkyl and  $\alpha$ -aryl- $\gamma$ -chlorobutyronitriles and alkyl and aryl substituted cyclopropyl cyanides were required. The present paper describes the preparation of one of the chloro and two of the cyclic compounds.

<sup>1</sup> This paper is from the first part of a thesis presented by Edwin Chandler Knowles in June, 1931, to the Graduate School of the Rensselaer Polytechnic Institute in partial fulfillment of the requirements for the degree of Doctor of Philosophy.