

The two cyclic hydrocarbons listed by Kierstead and Turkevich show

| | | | |
|--------------|-------|------|-------|
| Cyclopentane | 5.554 | 1878 | 70.13 |
| Cyclohexane | 15.21 | 2905 | 84.16 |

The rather rapid increase in energy of activation for viscous flow with only slight increase in molecular weights for the hydrocarbon series is contrasted with the much slower increase with larger members of the dimethylsiloxane polymer series.

Acknowledgments.—The authors wish to thank Mr. James H. McHard for his contribution to the analytical work, and Mr. R. F. Fleming

for valuable assistance in some of the early work on isolation of these compounds.

Summary

1. Cyclic dimethylsiloxane polymers from three to eight units have been prepared and their physical properties reported.

2. These cyclic structures may be isolated either from the hydrolysis products of dimethylsilane derivatives or by destructive distillation of dimethylsiloxane high polymers.

3. The phenomenally low molecular cohesion of dimethylsiloxanes compared with hydrocarbons is observed from surface tension values, vapor pressure data, and fluidity calculations.

MIDLAND, MICHIGAN

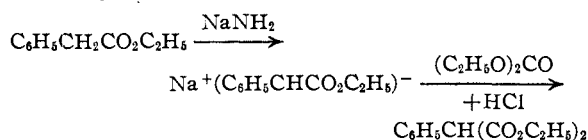
RECEIVED DECEMBER 13, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

The Carboethoxylation of Ethyl Phenylacetate and of Ethyl α -Phenyl-*n*-butyrate Using Sodium Amide¹

By HOWARD G. WALKER, JR., ROBERT LEVINE,² ROBERT F. KIBLER AND CHARLES R. HAUSER

Wallingford, Homeyer and Jones³ have shown that the carboethoxylation of ethyl phenylacetate with diethyl carbonate to form diethyl α -phenylmalonate may be effected in high yield by means of sodium ethoxide under forced conditions. We have found that this carboethoxylation may also be effected satisfactorily, and in considerably less time, by means of sodium amide. Since earlier workers⁴ have been unsuccessful in their attempts to effect the reaction using sodium amide, our method is worthy of comment. It consists of first converting ethyl phenylacetate to its sodium derivative in the presence of excess sodium amide in liquid ammonia, replacing the ammonia by ether and adding diethyl carbonate. In this manner the self-condensation of the ethyl phenylacetate, observed by the earlier workers,⁴ was avoided or at least minimized. The carboethoxylation may be represented, thus



In a similar manner the carboethoxylation of ethyl α -phenyl-*n*-butyrate has been effected by means of sodium amide to form diethyl α -phenyl- α -ethylmalonate. However, the yield with this ester has been somewhat lower than that obtained with ethyl phenylacetate. Wallingford,

Homeyer and Jones³ have shown that ethyl α -phenyl-*n*-butyrate fails to undergo carboethoxylation in the presence of sodium ethoxide, even under forced conditions.

The sodium derivative of ethyl α -phenyl-*n*-butyrate has also been treated with ethyl chlorocarbonate to form presumably diethyl α -phenyl- α -ethylmalonate. However, the yield was lower than that with diethyl carbonate and was considerably lower than that obtained in the somewhat similar reaction of ethyl chlorocarbonate with the sodium derivative of ethyl isobutyrate, prepared by means of sodium triphenylmethide.⁵

Since ethyl propionate and higher aliphatic esters react with sodium amide to form considerable amounts of the corresponding amides,⁶ no attempt has been made to carboethoxylate these esters using this base. Attempts have been made to carboethoxylate *n*-butyl and *t*-butyl acetates with diethyl carbonate using sodium amide but mixtures of condensation products appeared to be formed. Various aliphatic ethyl esters have been carboethoxylated using sodium ethoxide³ or sodium triphenylmethide.^{5,7}

Experimental

Diethyl α -Phenylmalonate.—Sodium amide (0.6 mole) was prepared in liquid ammonia as described previously.⁸ Ethyl phenylacetate (0.3 mole), dissolved in 100 cc. of absolute ether, was added over a period of two minutes. The reaction flask was placed on a steam-bath and the ammonia evaporated (this takes approximately fifteen minutes), sufficient absolute ether being added so that the contents of the flask remained at approximately 300 cc. As soon as the ether began to reflux, the steam-bath

(1) Paper XXXIII on "Condensations"; paper XXXII, THIS JOURNAL, **68**, 26 (1946).

(2) Present address: The Mathieson Alkali Works, Niagara Falls, New York.

(3) Wallingford, Homeyer and Jones, THIS JOURNAL, **63**, 2056 (1941).

(4) Nelson and Cretcher, *ibid.*, **50**, 2760 (1928).

(5) Hudson and Hauser, *ibid.*, **63**, 3156 (1941).

(6) Hauser, Levine and Kibler, *ibid.*, **68**, 26 (1946).

(7) Baumgarten and Hauser, *ibid.*, **66**, 1037 (1944).

(8) Levine and Hauser, *ibid.*, **66**, 1768 (1944).

was removed and 0.6 mole of diethyl carbonate, dissolved in 50 cc. of absolute ether, was added to the stirred reaction mixture as rapidly as the ether was efficiently condensed. The reaction mixture was again placed on a steam-bath and the mixture stirred and refluxed for two hours longer. The reaction mixture was poured into a mixture of 50 g. of ice and 100 cc. of concentrated hydrochloric acid and the phases separated. The ethereal phase was dried over Drierite, the solvent distilled and most of the diethyl carbonate distilled off at atmospheric pressure. The residue was fractionated *in vacuo*, collecting diethyl α -phenylmalonate, b. p. 127–130° at 2 mm.³; yield 64%.

Diethyl α -Phenyl- α -ethylmalonate.—The reaction of 0.1 mole of ethyl α -phenyl-*n*-butyrate, 0.2 mole of sodium amide and 0.2 mole of diethyl carbonate was carried out essentially as described above, except that the reaction mixture was refluxed for eight hours instead of two hours.⁹ The product, diethyl α -phenyl- α -ethylmalonate, boiled at 169–171° at 19 mm. in agreement with that reported in the literature⁴; yield 40%.

*Anal.*¹⁰ Calcd. for C₁₈H₂₀O₄: C, 68.12; H, 7.63. Found:

(9) When the reaction mixture was refluxed for two hours, the yield of carbethoxylation product was only 16%, 70% of the ester being recovered. No α -phenyl-*n*-butyramide was found in either of the carbethoxylation experiments. Ethyl α -phenyl-*n*-butyrate appears to be converted readily to its sodium derivative in the presence of sodium amide in liquid ammonia, since, when this ester is added to an equivalent of sodium amide in liquid ammonia containing a trace of sodium triphenylmethide as indicator,⁹ the deep red color of the mixture is discharged almost immediately.

(10) Microanalysis by Arlington Laboratories, Fairfax, Virginia.

C, 67.80; H, 7.84. A sample of the product was converted to phenobarbital, m. p. 173–174°, essentially as described by Nelson and Cretcher,⁴ except that Mathieson sodium methoxide was used instead of sodium ethoxide.

An ether suspension of the sodium derivative of ethyl α -phenyl-*n*-butyrate, prepared from 0.1 mole of the ester and 0.1 mole of sodium amide, was refluxed until essentially all of the ammonia had been driven off, and 15% excess of ethyl chlorocarbonate in 50 cc. of absolute ether was then added. After stirring for one hour, the mixture was shaken with ice and water. The ether phase was washed with sodium bicarbonate solution, dried with Drierite and the solvent distilled. The residue was fractionated, collecting the fraction boiling at 169–171° at 19 mm., presumably diethyl α -phenyl- α -ethylmalonate; yield 30%. The product was colored yellow. Similar results were obtained using a 100% excess of ethyl chlorocarbonate.

Summary

1. Ethyl phenylacetate and ethyl α -phenyl-*n*-butyrate have been carbethoxylated with diethyl carbonate by means of sodium amide to form diethyl α -phenylmalonate and diethyl α -phenyl- α -ethylmalonate, respectively.

2. The carbethoxylation of certain other esters is considered.

DURHAM, NORTH CAROLINA RECEIVED JANUARY 5, 1946

[CONTRIBUTION FROM THE ARMY INDUSTRIAL HYGIENE LABORATORY¹]

Preparation of 2,4,6-Trichlorophenyl Isocyanate

BY ROBERT R. McNARY² AND LOUIS MAGID³

In the course of a special investigation, it was desired to synthesize 2,4,6-trichlorophenyl isocyanate, and its corresponding methyl and ethyl alcohol derivatives, namely, 2,4,6-trichlorophenyl ethyl carbamate and 2,4,6-trichlorophenyl methyl carbamate. The preparation or properties of these compounds have not heretofore been reported in the literature.

The method used for the synthesis of 2,4,6-trichlorophenyl isocyanate was based upon the method developed for the preparation of *p*-nitrophenyl isocyanate by Shriner, Horne and Cox.⁴

Experimental

Preparation of 2,4,6-Trichlorophenyl Isocyanate. (Cl₃C₆H₂N=C=O) (mol. wt. 222.5).—Carbonyl chloride was prepared by the action of fuming sulfuric acid on carbon tetrachloride⁵ and then passed through concentrated sulfuric acid to remove the sulfur trioxide and sulfuryl chloride vapors. Seventy-five cc. of dry benzene was saturated with carbonyl chloride at room temperature and

a solution of 5 g. of 2,4,6-trichloroaniline in 25 cc. of dry benzene was run in slowly over a period of one hour. During this time a steady stream of carbonyl chloride was passed through the solution to ensure an excess. After the addition of the last of the trichloroaniline, the stream of carbonyl chloride was continued for five minutes and then shut off. The benzene solution was then filtered and quickly evaporated at room temperature with a stream of dry air. The residue was recrystallized from dry carbon tetrachloride and the product obtained in the form of white needles melting at 66–67° (uncor.).

Properties and Reactions of 2,4,6-Trichlorophenyl Isocyanate.—2,4,6-Trichlorophenyl isocyanate has a characteristic but not unpleasant odor. It sublimes on heating. It is not hygroscopic, but in contact with the moisture of the air, or when dissolved in undried organic solvents, 2,4,6,2',4',6'-hexachlorocarbonylurea (m. p. 320–325°, uncor.), which was first prepared by Chattaway and Orton,⁶ is formed. Trichlorophenyl isocyanate is insoluble in water but soluble in benzene, petroleum ether, ether, carbon tetrachloride, chloroform, mineral spirits, alcohol, methyl alcohol and acetone. On hydrolysis with water or aqueous alkaline solutions, 2,4,6-trichloroaniline and 2,4,6,2',4',6'-hexachlorocarbonylurea are formed. When dissolved in acetone and precipitated by the addition of water, the product formed is almost entirely 2,4,6-trichloroaniline. Trichlorophenyl isocyanate reacts with methyl and ethyl alcohols to form the corresponding urethans.

Preparation of 2,4,6-Trichlorophenyl Ethyl Carbamate. (Cl₃C₆H₂NHCOOC₂H₅) (mol. wt. 268.5).—When 2,4,6-trichlorophenyl isocyanate is dissolved in an excess of ethyl alcohol, 2,4,6-trichlorophenyl ethyl carbamate

(1) Present location: Edgewood Arsenal, Md.

(2) Present address: U. S. Citrus Products Station, Winter Haven, Florida.

(3) Present address: The Wm. S. Merrell Co., Cincinnati, 15, Ohio.

(4) R. L. Shriner, W. H. Horne and R. F. B. Cox, "Organic Syntheses," Vol. XIV, John Wiley and Sons, Inc., New York, N. Y., 1934, p. 72.

(5) H. Erdmann, *Ber.*, **26**, 1993 (1893).

(6) Chattaway and Orton, *ibid.*, **34**, 1077 (1901).