Vol. 68

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.

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### 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 Carbethoxylation of Ethyl Phenylacetate and of Ethyl $\alpha$ -Phenyl-*n*-butyrate Using Sodium Amide<sup>1</sup>

## BY HOWARD G. WALKER, JR., ROBERT LEVINE,<sup>2</sup> ROBERT F. KIBLER AND CHARLES R. HAUSER

Wallingford, Homever and Jones<sup>3</sup> have shown that the carbethoxylation of ethyl phenylacetate with diethyl carbonate to form diethyl  $\alpha$ -phenylmalonate may be effected in high yield by means of sodium ethoxide under forced conditions. We have found that this carbethoxylation may also be effected satisfactorily, and in considerably less time, by means of sodium amide. Since earlier workers<sup>4</sup> 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 carbethoxylation may be represented, thus

$$C_{6}H_{5}CH_{2}CO_{2}C_{2}H_{5} \xrightarrow{\text{NaNH}_{2}} Na^{+}(C_{6}H_{5}CHCO_{2}C_{2}H_{5})^{-} \xrightarrow{(C_{2}H_{6}O)_{2}CO} (C_{2}H_{5})^{-} \xrightarrow{(C_{2}H_{6}O)_{2}CO} (C_{2}H_{6})^{-} \xrightarrow{(C_{2}H_{6}O)_{2}CO} (C_{2}H_{6})$$

+HCl C<sub>6</sub>H<sub>5</sub>CH(CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>

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

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

Homeyer and Jones<sup>3</sup> have shown that ethyl  $\alpha$ -phenyl-*n*-butyrate fails to undergo carbethoxylation in the presence of sodium ethoxide, even under forced conditions.

The sodium derivative of ethyl  $\alpha$ -phenyl-*n*butyrate has also been treated with ethyl chlorocarbonate to form presumably diethyl  $\alpha$ -phenyl- $\alpha$ -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.<sup>5</sup>

Since ethyl propionate and higher aliphatic esters react with sodium amide to form considerable amounts of the corresponding amides,<sup>6</sup> no attempt has been made to carbethoxylate these esters using this base. Attempts have been made to carbethoxylate *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 carbethoxylated using sodium ethoxide<sup>3</sup> or sodium triphenylmethide.<sup>5,7</sup>

#### Experimental

Diethyl  $\alpha$ -Phenylmalonate.—Sodium amide (0.6 mole) was prepared in liquid ammonia as described previously.<sup>8</sup> 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

- (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).

672

<sup>(1)</sup> Paper XXXIII on "Condensations"; paper XXXII, THIS JOURNAL, 68, 26 (1946).

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<sup>(3)</sup> Wallingford, Homeyer and Jones, THIS JOURNAL, 63, 2056 (1941).

<sup>(5)</sup> Hudson and Hauser, ibid., 63, 3156 (1941).

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  $\alpha$ phenylmalonate, b. p. 127-130° at 2 mm<sup>3</sup>; yield 64%. Diethyl  $\alpha$ -Phenyl- $\alpha$ -ethylmalonate.—The reaction of

Diethyl  $\alpha$ -Phenyl- $\alpha$ -ethylmalonate.—The reaction of 0.1 mole of ethyl  $\alpha$ -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.<sup>9</sup> The product, diethyl  $\alpha$ -phenyl- $\alpha$ -ethylmalonate, boiled at 169–171° at 19 mm. in agreement with that reported in the literature<sup>4</sup>; yield 40%.

Anal.<sup>10</sup> Calcd. for C<sub>15</sub>H<sub>20</sub>O<sub>4</sub>: 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 *a*-phenyl-*n*-butyramide was found in either of the carbethoxylation experiments. Ethyl *a*-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, <sup>e</sup> 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.  $173-174^{\circ}$ , essentially as described by Nelson and Cretcher,<sup>4</sup> except that Mathieson sodium methoxide was used instead of sodium ethoxide.

An ether suspension of the sodium derivative of ethyl  $\alpha$ -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  $\alpha$ -phenyl- $\alpha$ -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  $\alpha$ -phenyl*n*-butyrate have been carbethoxylated with diethyl carbonate by means of sodium amide to form diethyl  $\alpha$ -phenylmalonate and diethyl  $\alpha$ phenyl- $\alpha$ -ethylmalonate, respectively.

2. The carbethoxylation of certain other esters is considered.

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[CONTRIBUTION FROM THE ARMY INDUSTRIAL HYGIENE LABORATORY<sup>1</sup>]

# Preparation of 2,4,6-Trichlorophenyl Isocyanate

### By Robert R. McNary<sup>2</sup> and Louis Magid<sup>3</sup>

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 pnitrophenyl isocyanate by Shriner, Horne and Cox.<sup>4</sup>

#### Experimental

Preparation of 2,4,6-Trichlorophenyl Isocyanate. (Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>N=C=O) (mol. wt. 222.5).—Carbonyl chloride was prepared by the action of fuming sulfuric acid on carbon tetrachloride<sup>5</sup> 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

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

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'-hexachlorocarbanilide (m. p.  $320-325^{\circ}$ , uncor.), which was first prepared by Chattaway and Orton,<sup>6</sup> Trichlorophenyl isocyanate is insoluble in is formed. 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'-hexachlorocarbanilide 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.  $(Cl_2C_6H_2NHCOOC_2H_\delta)$  (mol. wt. 268.5).—When 2,4,6-trichlorophenyl isocyanate is dissolved in an excess of ethyl alcohol, 2,4,6-trichlorophenyl ethyl carbamate

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

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<sup>(4)</sup> 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.