



The dehalogenated polymer (I) was shown to be resistant to ozone and permanganate but added chlorine on chlorination. On vigorous nitric acid oxidation, no products could be isolated that would have been characteristic of a dehydrohalogenated polymer.

The preparation of I was repeated in order to obtain additional evidence for the original structure designation and to investigate the position of characteristic cyclopropane bands in a polymer environment. Only 60% of the total chlorine was removed in our experiments, compared to 85% obtained in the previous work; but this seems sufficient for infrared analysis. Films of I were cast directly on salt plates from dioxane solution, dried *in vacuo*, and compared to films of polyvinyl chloride prepared in a like manner. The spectrophotometer was a Perkin-Elmer Model 21 with sodium chloride optics.

Two new bands appeared in I in positions expected from prior band assignments in nonpolymeric cyclopropane structures. A band at  $9.83\mu$ , characteristic of the nonsymmetrical ring deformations of cyclopropanes<sup>3,4</sup> and a band at  $3.2\mu$ , characteristic of the methylene hydrogens of a cyclopropane ring<sup>4,5</sup> confirm the original assignment. Bands associated with carbon-carbon double bonds were either not present or obscured by carbon-chlorine overtone bands between 6.0 and  $6.5\mu$  and past  $10\mu$  by various skeletal vibrations.

It was not possible to obtain interpretable nuclear magnetic resonance spectra of I because of its low solubility in organic solvents.

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ORGANIC CHEMICALS DEPARTMENT  
E. I. DU PONT DE NEMOURS & CO.  
WILMINGTON, DEL.

(3) J. M. Derfer, E. F. Pickett, and C. E. Boord, *J. Am. Chem. Soc.*, **71**, 2482 (1949).

(4) V. A. Slabey, *J. Am. Chem. Soc.*, **76**, 3604 (1954).

(5) S. E. Wiberley and S. C. Bunce, *Anal. Chem.*, **24**, 623 (1952).

### Metalation of Cyclopropane by Amylsodium<sup>1</sup>

EDWARD J. LANPHER, LESLIE M. REDMAN, AND  
AVERY A. MORTON

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Metalation of hydrocarbons has been observed only when some unsaturation was present, a pre-

vious success with decalin<sup>2</sup> having been found due to some impurity.<sup>3</sup> The first experiments with cyclopropane were carried out about ten years ago in the presence of isopropoxide with the expectation that the ring would open to give allylsodium. Thereby an alternative method for the preparation of an Alfin catalyst<sup>4,5</sup> would be provided. The product of this reaction, however, did not cause Alfin polymerization of butadiene. Carbonation yielded an acid which did not resemble vinylacetic but was similar to cyclopropanecarboxylic acid.

Recently cyclopropane was again metalated, but in the absence of an alkoxide, in order to study the absorption spectrum for the cyclopropyl anion. The infrared spectrum showed bands not far from those of cyclopropane itself and entirely distinct from those for allylsodium or amylsodium. Carbonation produced cyclopropanecarboxylic acid which was converted to the known amide for identification.

Although cyclopropane has a formula in which all four valencies for each carbon appear saturated, it still possesses a fair degree of olefinic character according to Coulson and Moffit<sup>6</sup> and Vogel.<sup>7</sup> Accordingly the statements previously made to the effect that some unsaturated system was necessary<sup>8</sup> for metalation of a hydrocarbon and that no indiscriminate removal of hydrogen by a supposedly all-powerful anion<sup>9</sup> took place are still valid.

### EXPERIMENTAL

*Metalation in the presence of isopropoxide.* Amylsodium was prepared<sup>10</sup> from 1 g.-atom of sodium and 0.5 mole of amyl chloride in the usual manner. Isopropyl alcohol (15 ml.) was added and 15 min. later the mixture was saturated with cyclopropane. All operations were under an atmosphere of dry nitrogen and the mixture was continuously stirred at 5000 r.p.m. After a total time of 6.5 hr. the reaction mixture was transferred to a bottle and stored under nitrogen. A portion (20 ml. of suspension) was tested as a polymerizing agent for 30 ml. of butadiene in 180 ml. of pentane, but did not produce the thick gel characteristic for Alfin polybuta-

(1) This work was performed as a part of research projects sponsored by the Reconstruction Finance Corp., Office of Synthetic Rubber, and by the National Science Foundation.

(2) A. A. Morton, J. B. Davidson, T. R. P. Gibb, Jr., E. L. Little, Jr., E. W. Clarke, and A. J. Green, *J. Am. Chem. Soc.*, **64**, 2250 (1942).

(3) A. A. Morton and S. M. Bloom, *J. Am. Chem. Soc.*, **76**, 2976 (1954).

(4) A. A. Morton, E. E. Magat, and R. L. Letsinger, *J. Am. Chem. Soc.*, **69**, 950 (1947).

(5) A. A. Morton, I. Nelidow, and E. Schonberg, Proc. Third Rubber Technology Conference, (1954) 108.

(6) C. A. Coulson and W. E. Moffit, *J. Chem. Phys.*, **15**, 151 (1947); *Phil. Mag.*, **40**, 1 (1949).

(7) E. Vogel, *Fortschr. chem. Forsch.*, **3**, 430 (1955).

(8) A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **21**, 93 (1956).

(9) A. A. Morton and A. F. Brachman, *J. Am. Chem. Soc.*, **76**, 2973 (1954).

(10) A. A. Morton, F. D. Marsh, R. D. Coombs, A. L. Lyons, S. E. Penner, H. E. Ramsden, V. B. Baker, E. L. Little, Jr., and R. L. Letsinger, *J. Am. Chem. Soc.*, **72**, 3785 (1950).

diene. No marked polymerization took place within 1 hr. The remainder of the blue-black mixture was carbonated. The carboxylic acid therefrom distilled at 69–86°/1 mm. The neutralization equivalent was 76 and the refractive index was 1.4362. The yield was 1.3 g.

*Metalation in the absence of alkoxide.* A suspension (250 ml.) of amylsodium was prepared in the usual way<sup>10</sup> from 0.5 g.-atoms of sodium sand and 0.25 mole of amyl chloride, and, next, was saturated with cyclopropane and allowed to stand. The disappearance of amylsodium was followed by infrared measurements<sup>11,12</sup> of a Nujol mull. After one week the bands at 919 and 755  $\text{cm.}^{-1}$  characteristic for the amyl anion had become very much weaker. Meanwhile strong absorption bands had appeared at 1155, 1055, 1030, 860, and 810  $\text{cm.}^{-1}$ ; a moderate one at 1570  $\text{cm.}^{-1}$  and a weak band at 745  $\text{cm.}^{-1}$ . These bands are not far from some of those for cyclopropane itself which were very strong at 1434, 1024, and 866, moderate at 1510 and 1188, and very weak at 745  $\text{cm.}^{-1}$ . The bands are different from those for the allyl ion<sup>12</sup> which are very strong at 1525, 1247, and 600  $\text{cm.}^{-1}$ .

From this reaction mixture a 25-ml. aliquot was evaporated to dryness under reduced pressure. Then the dried residue was heated to 100° for 1 hr. The condensate caught in a nitrogen cooled trap showed an absorption curve identical with that for cyclopropane itself except for contamination from the pyrolysis of some amylsodium which was still present.

The remainder of the reaction mixture was carbonated and the recovered acids fractionated. The fraction of impure acid (4.4 g.), collected at 90°/30 mm., had  $n_D^{25}$  1.4355. The recorded<sup>13</sup> refractive index for cyclopropanecarboxylic acid is  $n_D^{25}$  1.4359, and boiling point is 105°/48 mm. The amide from the acid chloride and ammonia melted at 124–127° (recorded<sup>14</sup> 124.5–126°).

DEPARTMENT OF CHEMISTRY  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
CAMBRIDGE 39, MASS.

(11) E. J. Lanpher, *J. Org. Chem.*, **21**, 830 (1956); *J. Am. Chem. Soc.*, **79**, 5578 (1957).

(12) E. J. Lanpher, *J. Am. Chem. Soc.*, **79**, 5578 (1957).

(13) J. D. Roberts, *J. Am. Chem. Soc.*, **73**, 5030 (1951).

(14) N. J. Demjanow and M. Dojasenko, *Ber.*, **56**, 2200 (1923).

## A Synthesis of Fluorene-3-carboxylic Acid<sup>1</sup>

D. C. MORRISON

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Alder<sup>2</sup> and coworkers have shown that the sulfuric acid cyclization of phenyl terephthalic acid (diphenyl 2-5-dicarboxylic acid) gives fluorenone-3-carboxylic acid. Their synthesis of the diphenyl dicarboxylic acid, however, presents several difficulties and it was thought that if this acid were more readily available, a convenient route to 3-substituted fluorenes would be at hand. In the present work, the ester of phenyl terephthalic acid was prepared by a one-step process from diethyl terephthalate, though in mediocre yield.

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(2) K. Alder, K. Heimbach, and K. Neufang, *Ann.*, **586**, 138 (1954); *Chem. Abstr.*, **49**, 5396 (1955).

Hey<sup>3</sup> has demonstrated that the free radical decomposition of dibenzoyl peroxide in ethyl benzoate yields a mixture of esters of phenyl benzoic acids. In a similar reaction with diethyl terephthalate, only one isomer is possible due to the symmetry of para di-substituted benzenes. This operation has now been carried out yielding the ester of the desired phenyl terephthalic acid in about 12% yield. The poor yields (expected in this type of reaction) are compensated for by the economy of starting materials. The ester was hydrolyzed under alkaline conditions to the phenyl terephthalic acid which was cyclized by sulfuric acid to the fluorenone-3-carboxylic acid.<sup>2</sup> The latter was purified through its methyl ester as was done by Campbell and Stafford.<sup>4</sup> Reaction of the methyl ester with red phosphorus and hydriodic acid in glacial acetic acid caused reduction and hydrolysis to give fluorene-3-carboxylic acid. This acid was further characterized by its methyl ester.

The route to fluorenone-3-carboxylic acid by oxidation of 3-methyl fluorene by permanganate<sup>5</sup> or by chromic acid<sup>6</sup> gave poor yields of material which was difficult to purify due to its contamination with acids probably produced by further oxidation of the desired acid (with cleavage of the fluorene ring).

## EXPERIMENTAL

Melting points are uncorrected.

The better known dimethyl terephthalate was not employed in the reaction as it is a solid at steam bath temperatures. The diethyl terephthalate was made by two days refluxing of the acid with sulfuric acid and ethanol, followed by conventional purification.

*Diethyl phenylterephthalate.* Diethyl terephthalate (260 g.) was melted and kept at 60–70° while 50 g. of dibenzoyl peroxide were added in portions. The solution was immersed in a bath of boiling water for 4 hr. and then excess diethyl terephthalate was distilled under vacuum directly from the flask. If the temperature during the first hour of the reaction should rise above 100°, the decomposition may become violent. The distillation was carried out at 5 mm. and a forerun of diphenyl was discarded. This was followed by a large amount of recovered terephthalate which could be used again in another run. A similar reaction was done using 357 g. of diethyl terephthalate and 60 g. of dibenzoyl peroxide, and the distillation residues combined with those from the first run. These were now dissolved in ether and the solution extracted with aqueous sodium carbonate and then washed with sodium chloride solution (if water is used, a stable emulsion results). The ether was distilled and the product taken at 140–195°/3 mm. It was redistilled at about 160°/3 mm. The yield was 31.76 g. of a light yellow viscous oil. This is 11.73% based on the peroxide. The yield may perhaps be improved by reaction at higher dilution or by better temperature control. A resinous residue is left in the distillation flask.

*Phenyl terephthalic acid.* The 31.76 g. of ester was refluxed for 32 hr. with 40 g. of potassium hydroxide in 50% ethanol and the acid isolated as usual, by acidification with hydro-

(3) D. H. Hey, *J. Chem. Soc.*, 1966 (1934).

(4) N. Campbell and W. H. Stafford, *J. Chem. Soc.*, 299 (1952).

(5) D. Vorlander and A. Pritsche, *Ber.*, **46**, 1793 (1913).

(6) O. Kruber, *Ber.*, **65**, 1395 (1932).