CHARACTERISTICS OF DIALKYL ALKYLTHIOBORONATES AND TRIALKYLBORATES

Compound	Yield, %	B.p. (mm.), °C.
Ethylene *n*-butyl thioboronate	45	84 (6)
Ethylene *i*-butyl thioboronate	38	83 (6.5)
Di-*n*-amyl-*n*-butyl thioboronate	29	132 (0.5)
Di-*n*-amyl-*t*-butyl thioboronate	72	122 (0.2)
Di-*n*-butyl-*s*-butyl thioboronate	63	105 (0.8)
Di-*n*-butyl-*n*-hexyl thioboronate	58	119 (0.3)
Tri-*n*-amyl thioborate	65	164 (0.4)
Tri-*n*-butyl thioborate	70	147 (1.0)

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RECEIVED DECEMBER 17, 1959

A NEW METHOD FOR THE PREPARATION OF CRYSTALLINE POLYVINYL CHLORIDE

Sir:

We have prepared crystalline polyvinyl chloride with conventional free-radical catalysts at 50° using aliphatic aldehydes as polymerization media. Although all aliphatic aldehydes tried have produced this stereoregulating effect, *n*-butyraldehyde and 2-ethylhexylaldehyde appear to give the best results. As is to be expected from the chain transfer activity of aldehydes, very low molecular weight polymers are produced, *e.g.*, approximately 5,000. The reaction is carried out at 50° using a mole to mole ratio of monomer to aldehyde and a millimole of free-radical catalyst per mole of monomer. A typical polymerization using 72.0 g. of *n*-butyraldehyde, 62.5 g. of vinyl chloride, and 0.16 g. of azodiisobutyronitrile in 9 hours yields 9.13 g. of polyvinyl chloride. The crystalline material in tetrahydrofuran gives a cloudy solution which does not clear up on heating. The same effect is noted with cyclohexanone but on heating to 120° the solution becomes clear.

The crystallinity, and hence stereoregularity, of the polymers was investigated using X-ray diffraction and infrared absorption methods. The regular sequences in polyvinyl chloride crystallize readily so that changes in crystallinity are directly related to changes in regularity. The unoriented X-ray pattern of the polyvinyl chloride prepared in *n*-butyraldehyde possesses sharp lines with "d" spacings at 5.16 (m), 4.66 (s), 3.65 (m), 3.44 (m), 2.84 (m), 2.56 (w), 2.28 (m), 2.07 (w), 1.78 (vw), 1.59 (vw), 1.40 (vw), 1.25 (vw), 1.14 (vw) Å. (letters in parentheses indicate relative intensities where s = strong, m = medium, w = weak, vw = very weak). These values agree well with those reported by Fordham, Burleigh and Sturm.[1] The lines with "d" spacings at 3.65, 1.40, 1.25, and 1.14 Å., however, have not been reported previously.

With regard to the infrared absorption spectrum of polyvinyl chloride, the ratio of the absorbance at 635 cm.$^{-1}$ to that at 692 cm.$^{-1}$ has been used as a measure of crystalline syndiotactic units in the polymer.[2-6] Table I gives the D_{635}/D_{692} ratio for polyvinyl chloride prepared in bulk at high and low temperatures and in *n*-butyraldehyde at high temperature.

TABLE I

INFRARED ABSORPTION DATA

Polyvinyl Chloride Prepared in	D_{635}/D_{692}
Bulk at +50°	1.5
Bulk at −70°	2.6
n-Butyraldehyde at +50°	4.3

An increase in the absorbance ratio is indicative of increased crystallinity. The infrared absorption measurements were made using films cast on potassium bromide discs from tetrahydrofuran or cyclohexanone solutions; for the polymer prepared in *n*-butyraldehyde the film was cast from a cyclohexanone solution at 120°. Based on the above evidence, we have assigned the syndiotactic structure to this polyvinyl chloride.

The stereoregulating effect of aliphatic aldehydes on the free-radical polymerization of vinyl chloride is not yet understood. Study of the mechanism of this effect is in progress.

Acknowledgments—The author is grateful to I. E. Smiley for the X-ray diffraction data and J. J. Mannion for the infrared absorption measurements.

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RECEIVED DECEMBER 4, 1959

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(1) J. W. L. Fordham, P. H. Burleigh, and C. L. Sturm, Abstracts 135th A.C.S. Meeting, Boston, April, 1959.

(2) S. Mizushima, T. Shimanouchi, K. Nakamura, M. Hayashi, and S. Tsuchiya, *J. Chem. Phys.*, **26**, 970 (1957).

(3) R. J. Grisenthwaite and R. F. Hunter, *Chem. & Ind.*, 433 (1959).

(4) S. Krimm, A. R. Berens, V. L. Folt and J. J. Shipman, *ibid.*, 433 (1959).

(5) T. Shimanouchi, S. Tsuchiya and S. Mizushima, *J. Chem. Phys.*, **30**, 1365 (1959).

(6) S. Krimm, *Society of Plastic Engineers Journal*, (Sept.) 797 (1959).

A NOVEL SYNTHESIS OF BENZOCYCLOBUTENE DERIVATIVES[1]

Sir:

About a year ago we reported[2] the formation of a stable dipositive carbonium ion from trichloromethylpentamethylbenzene (I). We now wish to record another unusual and useful reaction of this and related substances.

I is a colorless, crystalline solid, m.p. 94.5–95.0°. It was observed that at or slightly above its melting point, *I evolved hydrogen chloride.* In a quantitative experiment, 1.074 g. (4.05 mmoles) of I was heated at 110–125° in a dry nitrogen stream which subsequently passed through standard sodium hydroxide. In the first hour, 3.76 mmoles of hydrogen chloride was collected. Two more hours netted 0.50 mmole, and after three additional hours, only 0.03 mmole more of hydrogen chloride was produced (a total of 105.9% of the theoretical for one mole). On cooling, there was isolated a crystalline solid II, m.p. 73–74° (from pentane). *Anal.*[3] Calcd. for $C_{12}H_{14}Cl_2$:

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research, under grant 488-C.

(2) H. Hart and R. W. Fish, THIS JOURNAL, **80**, 5894 (1958). A detailed report of this work is in preparation.

(3) All analyses by Spang Microanalytical Laboratory, P. O. Box 1111, Ann Arbor, Michigan.

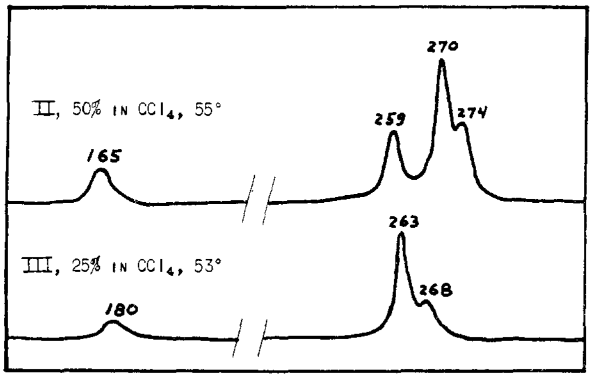
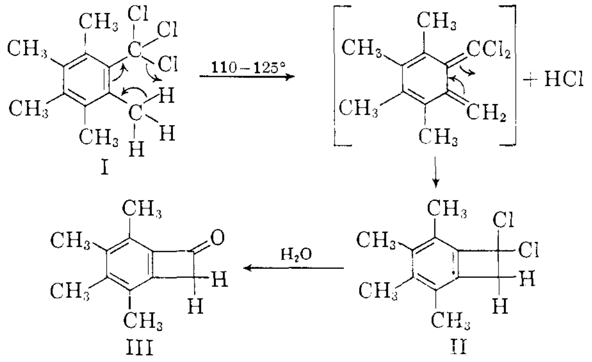


Fig. 1.—Nuclear magnetic resonance spectra at 60 Mc.: numbers are cps. with respect to benzene as an external reference.

C, 62.89; H, 6.16; Cl, 30.95; mol. wt., 229. Found: C, 62.93; H, 6.27; Cl, 30.88; Rast molecular weight (camphor), 201. II gave an immediate precipitate with aqueous-alcoholic silver nitrate; after removing the silver chloride, work-up of the filtrate, or alternatively by direct hydrolysis of II with aqueous acetone, there was obtained in excellent yield a crystalline ketone III, m.p. 153–154° (from ethanol). *Anal.* Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.57; H, 8.16. Oxime, m.p. 173–175°, 2,4-DNP, m.p. 282–283°. III had a carbonyl band at 5.67μ and bands in the ultraviolet (ethanol) at 306 mμ (log ϵ = 3.47) and 265 mμ (log ϵ = 4.18). The n.m.r. spectra of II and III are shown in the figure.[4]

These data are best interpreted in terms of the reaction scheme



From mesitylene, one can obtain a compound presumably analogous to II, m.p. 55–57° (from hexane). *Anal.* Calcd. for $C_{10}H_{10}Cl_2$: C, 59.72; H, 5.01; Cl, 35.26. Found: C, 59.90; H, 5.10; Cl, 35.27.

In a preparative scale experiment, without purification of the intermediate II, an 89% yield of III was obtained from 5 g. of I. This constitutes, then, an excellent preparative procedure for benzocyclobutenones and compounds derived therefrom.[5]

Its synthetic utility and the chemistry of the products are being explored.[6,7]

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[4] We are indebted to Mr. James C. Woodbrey for determining these spectra.

[5] For other benzocyclobutene syntheses, see M. P. Cava and A. A. Deana, THIS JOURNAL, **81**, 4266 (1959), and earlier papers by Cava's group; L. Horner, W. Kirmse and K. Muth, *Chem. Ber.*, **91**, 430 (1958); A. P. terBorg and A. F. Bickel, *Proc. Chem. Soc.*, 283 (1958); and F. R. Jensen and W. E. Coleman, *J. Org. Chem.*, **23**, 869 (1958).

[6] The results of a preliminary deuterium exchange experiment with III are of some interest. III (0.397 g., 1.50 mmoles) dissolved in 4 ml. of D_2O and 6 ml. of ethanol was refluxed for two hours. A 4-ml. sample was quenched in 20 ml. of ice-cold distilled water, and extracted immediately with three 10-ml. portions of pentane. Recovery of III was nearly quantitative; the crystalline product showed considerable C-D absorption at 4.48μ; the carbonyl at 5.7μ was unaltered.

[7] We are indebted to Mr. Frank J. Chloupek for stimulating discussions of this work.

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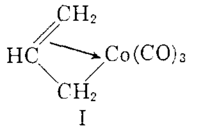
RECEIVED DECEMBER 23, 1959

ALLYLCOBALT CARBONYLS

Sir:

We wish to report the formation of a new type of cobalt carbonyl compound, allylcobalt tricarbonyl. When excess $NaCo(CO)_4$ reacts with allyl bromide in ether at 25°, exactly one mole of carbon monoxide is liberated per mole of bromide. Distillation yields a reddish yellow, air-sensitive liquid which can be crystallized from pentane to give a yellow crystalline solid, m.p. −33 to −32°.

Anal. Calcd. for $C_6H_5O_3Co$: CO, 45.6; Co, 32.0. Found CO (by treatment with I_2 in methanol), 44.8; Co, 31.5, 31.1. The compound was shown to be diamagnetic by e.p.r. The n.m.r. spectrum of the allyl compound shows three types of hydrogen in the ratio 2:2:1. Although the spectrum was not sufficiently well resolved to differentiate unequivocally between the unsymmetrical structure I and the symmetrical structure II, the preponderance of evidence would appear to favor the symmetrical structure.[1] Whereas alkylcobalt tetracarbonyls are quite unstable thermally,[2,3] allylcobalt tricarbonyl appears to be stable indefinitely at room temperature.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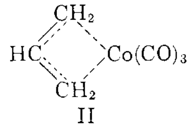
II

The equilibrium mixture of 1-bromo-2-butene and 3-bromo-1-butene reacts with $NaCo(CO)_4$ in an entirely analogous fashion. One mole of carbon monoxide is evolved and distillation yields a red-yellow oil identical with the reaction product of butadiene and $HCo(CO)_4$.[4,5] The compound is presumably 2-butenylcobalt tricarbonyl.[6]

If the reaction of allyl bromide with $NaCo(CO)_4$ is carried out at 0° in the presence of carbon monoxide, about 0.5 mole of carbon monoxide is absorbed. At this point the infrared spectrum of the solution shows a band at 5.8 μ, indicating the presence of an acylcobalt compound.[3] Gas is

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[1] We are indebted to Dr. J. C. W. Chien for the determination and interpretation of the e.p.r. and n.m.r. spectra.

[2] W. Hieber, O. Vohler and G. Braun, *Z. Naturforsch.*, **13b**, 192 (1958).

[3] R. F. Heck and D. S. Breslow, unpublished work.

[4] H. B. Jonassen, R. I. Stearns, J. Kenttämaa, D. W. Moore and A. G. Whittaker, THIS JOURNAL, **80**, 2586 (1958).

[5] W. W. Prichard, U. S. Reissue 24,653 (1959).

[6] H. B. Jonassen independently has arrived at the same conclusion (London Conference on Coördination Chemistry, April, 1959).