nance stabilized radical, whereas there is only one such position in the allyl ester.

The homopolymer formed by heating erythryl divalerate at 80° in the presence of 5% of benzoyl peroxide was a viscous liquid with a degree of polymerization of about 5. Since the homopolymer of erythryl diacetate[2] had a D.P. of 17.7, it appears that increasing the size of the acid residues decreases the molecular weight of erythryl ester polymers. The same trend was noted[4] in comparing the homopolymers of allyl acetate and allyl propionate (of D.P. 12 and 10, respectively). The very low molecular weight of the polyerythryl divalerate is in accord with the kinetic evidence for the occurrence of extensive degradative attack in the case of the erythryl ester.

A brief study of the copolymerization of erythryl divalerate with styrene gave results (shown in Table II) which are similar to those obtained with other saturated erythryl esters.[2] For example, copolymers of erythryl diacetate and styrene prepared from 1:1 and 1:1.7 monomer mixtures (molar ratios of ester to styrene) had ester to styrene ratios of 1:22 and 1:17, respectively.

TABLE II

COPOLYMERIZATION OF ERYTHYL DIVALERATE WITH STYRENE AT 80° FOR 48 HOURS USING 5% INITIATOR

Run	A	B	C
Ester:styrene in charge,[a] moles	1:2	1:1	1:2
Yield of polymer,[b] %	47	25	46
Melting range[c] of polymer, °C.	100–126	94–118	100–126
Chlorine in polymer, %	..	5.0	1.8
Sapn. no. of polymer	48.6	63.3	46.0
Ester:styrene in polymers,[d] moles	1:23	1:20	1:25

[a] Total weight of monomers, about 14 g. per run. Initiator, benzoyl peroxide in A, p-chlorobenzoyl peroxide in B and C. [b] Based on total monomers. [c] From first sintering point to free flow in a 1-mm. capillary melting point tube. [d] Values corrected for presence of p-chlorobenzoyl groups in polymer.

Experimental

Erythryl Divalerate.—This ester was prepared according to the method of Whitmore and Krems,[5] using erythrol and n-valeryl chloride (Eastman Kodak Co.). The erythrol was made from butadiene monoxide[6] obtained by a modification of the method of Kadesch.[7] The average yield of erythryl divalerate from four preparatory runs was 39.4% of product, b.p. 127° at 2 mm., $n^{20}D$ 1.4378; acid no., 0; peroxide no., 0; iodine no., 99.8 (calcd. 99.1); sapn. no., 428 (calcd. 438).

Kinetic Studies.—Tubes containing 2 to 3 g. of a solution of recrystallized benzoyl peroxide (99.5% pure by iodimetric analysis) and erythryl divalerate were sealed under nitrogen and heated at 80 ± 0.7°. After varying periods of time (shown in Fig. 1) the tubes were removed from the bath, chilled, and duplicate samples removed for determination of residual monomer by the catalytic Wijs method[8] and for peroxide by the iodimetric method of Nozaki.[9] Control experiments showed both methods to be accurate to within 1% for solutions containing up to 10% of benzoyl peroxide in the ester.

(5) W. F. Whitmore and I. J. Krems, THIS JOURNAL, 71, 2427 (1949).

(6) Pariselle, Ann. chim. phys., 8, 24, 389 (1911).

(7) R. G. Kadesch, THIS JOURNAL, 68, 41 (1946).

(8) H. D. Hoffman and C. E. Green, Oil and Soap, 16, 239 (1939).

(9) K. Nozaki, Ind. Eng. Chem., Anal. Ed., 18, 583 (1946).

Homopolymerization.—Two samples of erythryl divalerate (of total weight 19 g.) containing 5% by weight of benzoyl peroxide were heated at 80° for 48 hr. in sealed tubes containing high purity nitrogen. The combined contents were then dissolved in benzene, and freed from peroxides by three washings with 9% sodium carbonate followed by salt solution and water. After removal of the solvent, the unchanged monomer was distilled off at 3 mm. pressure. The residue was a viscous liquid, obtained in 65% yield, which could not be solidified nor further purified. The recovery of monomer was 21%.

Anal. Calcd. for $C_6H_5COO(C_{14}H_{24}O_4)_5$: mol. wt.. 1403; iodine no., 0; sapn. no., 439.1. Found: mol. wt. (CCl₄, b.p.), 1452; iodine no., 5.6; sapn. no., 491.5.

Copolymerization.—Copolymers of erythryl divalerate and styrene,[10] prepared as indicated in Table II, were freed from initiator as above and the solid polymers precipitated from benzene with methanol. The composition of the copolymers was determined from saponification analyses, with correction for the probable content of saponifiable initiator groups. The assumption was made that 60% of the chloride-containing groups in copolymers prepared with p-chlorobenzoyl peroxide consisted of p-chlorobenzoate groups. This is based on the findings of Bartlett and Altschul.[3] When benzoyl peroxide was the initiator, it was assumed that the same proportionate amount of saponifiable initiator residues could be present.

(10) Supplied through the courtesy of the Dow Chemical Co.

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The Thermal Decomposition of the Bis-pyridinium Salts of Tetramethylene and Pentamethylene Dibromides

BY ROBERT E. LYLE AND JOHN J. GARDIKES

The reaction of tetramethylene dibromide or pentamethylene dibromide with pyridine has been reported by Hartwell and Pogorelskin[1] to yield hygroscopic solids. The bromides could not be characterized as the anhydrous salts except by conversion to tetramethylene-α,δ-bis-pyridinium perchlorate and pentamethylene-α,ϵ-bis-pyridinium perchlorate. Gautier and Renault[2] obtained from the reaction of tetramethylene dibromide with pyridine a crystalline salt of well-defined melting point, but these authors failed to report any analyses for the compound.

In the repetition of this work, treatment of the dihalides with pyridine either with or without methanol as solvent yielded crystalline salts which were stable to the atmosphere for several weeks. The compound I formed from tetramethylene dibromide was identical with that reported by Gautier and Renault,[2] and analysis of the products from both reactions indicated that only the bis-pyridinium bromides had been formed. Limiting the quantity of pyridine to a 1:1 molar ratio also produced only the bisquaternary salts and no monoaddition salt could be isolated.

The thermal decomposition of alkyl pyridinium salts leads normally to the removal of pyridine hydrobromide producing the corresponding alkene. On heating these salts at 230–270°, two moles of pyridine hydrobromide were lost and compound I yielded butadiene while pentamethylene-α,ϵ-bis-

(1) J. L. Hartwell and M. A. Pogorelskin, THIS JOURNAL, 72, 2040 (1950).

(2) J. A. Gautier and J. Renault, Compt. rend., 225, 682 (1947).

pyridinium bromide (II) produced 1,3-pentadiene. Both dienes were identified as the tetrabromo derivatives.

Experimental

Preparation of the Bis-pyridinium Salts.—Dry pyridine was added to a solution of the dihalide in absolute methanol in slight excess of two moles of pyridine to one of the dihalide. The solution was allowed to stand for two days and the methanol distilled. The solid which crystallized was removed by filtration, washed with ether and recrystallized from absolute ethanol and ether or acetone. A quantitative yield of the salts was obtained.

The bis-pyridinium salt I of tetramethylene dibromide melted at 237–239° (lit.[2] m.p. 239°) after drying for one hour at 100° under reduced pressure.

Anal. Calcd. for $C_{14}H_{18}Br_2N_2$: Br, 42.74. Found: Br, 42.35.

The bis-pyridinium salt II of pentamethylene dibromide melted at 193–195° after drying as above.

Anal. Calcd. for $C_{15}H_{20}Br_2N_2$: Br, 41.18. Found: Br, 41.14.

The Thermal Decomposition of the Salts.—The bis-pyridinium salt was heated by a Woods metal-bath at 230–270° in a distilling flask connected through a trap at 0° to a receiver immersed in an acetone–Dry Ice-bath. A higher temperature increased the speed of the decomposition, but the distillate became contaminated with pyridine hydrobromide. The solid which remained in the distilling flask after the reaction was complete was recrystallized from absolute methanol and ether and melted at 212–215°; lit.[3] m.p. for pyridine hydrobromide, 213°.

Anal. Calcd. for C_5H_6BrN: Br, 49.94. Found: Br, 50.65.

Pyridine hydrobromide was recovered in quantitative yield from the decomposition of both salts.

The distillate (0.9 g.) from the decomposition of 10 g. of I was distilled into a solution of chloroform and bromine. After removal of the excess solvent, the solid was recrystallized from low-boiling petroleum ether yielding 3.1 g. (36% from I) of 1,2,3,4-tetrabromobutane, m.p. 115–116.8°; lit.[4] m.p. 118–119°. A mixed melting point with an authentic sample showed no depression.

Redistillation of the products from the decomposition of 39 g. of II yielded 5 g. (73% assuming 1,3-pentadiene) of a fraction boiling at 41–44°, n^{21}D 1.4310; lit.[5] b.p. 43–44°, n^{20}D 1.4314.

In order to prove the location of the double bonds, the diene was converted to the tetrabromo derivative by treatment with bromine in carbon tetrachloride. After recrystallization from ethanol, 1,2,3,4-tetrabromopentane melted at 113.4–114.4°; lit.[5] m.p. 114°.

(3) I. M. Heilbron, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, New York, N. Y., 1938, p. 553.

(4) I. M. Heilbron, ref. 3, p. 672.

(5) L. E. Schniepp and H. H. Geller, THIS JOURNAL, **67**, 54 (1945).

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Reaction of Grignard Reagents with Alkoxysilanes at Elevated Temperatures

BY E. T. McBEE, C. W. ROBERTS, G. F. JUDD AND T. S. CHAO

The first fluorine-containing difunctional silane, bis-(3,3,4,4,5,5,5-heptafluoropentyl)-diethoxysilane, was prepared in this Laboratory[1] by treating ethyl silicate with 3,3,4,4,5,5,5-heptafluoropentylmagnesium bromide. Subsequent work indicated that large quantities of this compound could not be obtained efficiently by this procedure. Appreci-

(1) O. R. Pierce, E. T. McBee and R. E. Cline, THIS JOURNAL, **75**, 5618 (1953).

able quantities of tetrakis-(3,3,4,4,5,5,5-heptafluoropentyl)-silane and tris-(3,3,4,4,5,5,5-heptafluoropentyl)-ethoxysilane were obtained with small yields of 3,3,4,4,5,5,5-heptafluoropentyltriethoxysilane. Since tetrasubstitution occurred preferentially under the original reaction conditions, it seemed reasonable that a higher temperature and a high concentration of the alkoxysilane would produce the monosubstituted product exclusively. This has been realized, both with fluorine-containing and non-fluorine-containing Grignard reagents. Methylmagnesium bromide, with a fifteen-fold excess of ethyl silicate gave a 68% yield of methyltriethoxysilane, whereas at the temperature of refluxing ether and a 2.38 mole ratio of reactants, only 12% of the product was obtained. 3,3,3-Trifluoropropylmagnesium chloride reacted with methyl silicate to give 95% of the monosubstituted product.

An additional factor in these displacement reactions is the complexing or adsorption of the products by magnesium ethoxy bromide. This loss of the silanes was lessened by adding excess ethyl silicate, which preferentially complexed with the magnesium salts.

Experimental[2]

Methyltriethoxysilane.—Methylmagnesium bromide (0.499 mole) was added dropwise over two hours to 1560 g. (7.5 moles) of ethyl silicate maintained at 105 ± 3°; the ether was removed as the reaction proceeded. The precipitate formed during the reaction was removed by filtration at 0°, and rectification of the filtrate through a 3' Heligrid-packed Todd column gave 2.7 g. (5.27%) of dimethyldiethoxysilane,[3] b.p. 111°, n^{20}D 1.3829, and 60 g. (67.5%) of methyltriethoxysilane, b.p. 143–146°, n^{20}D 1.3829. When this reaction was conducted at the temperature of refluxing ether, only 12% of methyltriethoxysilane was produced.

Dimethyldiethoxysilane.—Methylmagnesium bromide (107 ml., 0.1 mole) was added dropwise during 1.5 hr. to 43.4 g. (0.238 mole) of methyltriethoxysilane maintained at 93 ± 15° in a 250-ml. 3-necked flask fitted as described in the previous experiment. Ether was removed by distillation, benzene was added, and 14.9 g. of solid was removed by centrifugation. Rectification of the filtrate through a 3' glass spiral-packed Todd column gave 11.2 g. (76%) of dimethyldiethoxysilane, b.p. 69.5° (179 mm.), n^{29}D 1.3824.[4]

3,3,4,4,5,5,5-Heptafluoropentyltriethoxysilane.—A solution of 150 ml. (0.50 N, 0.075 mole) of 3,3,4,4,5,5,5-heptafluoropentylmagnesium bromide in ether was added dropwise during 3 hr. to 156 g. (0.75 mole) of ethyl silicate at 95–130°; the ether was stripped off through an 18" glass helices-packed column during the addition. The suspension was cooled in an ice-bath and filtered by suction, the flask being cooled in Dry Ice; the pentane was removed, and the residue rectified to give 19 g. (71%) of 3,3,4,4,-5,5,5-heptafluoropentyltriethoxysilane, b.p. 47° (3 mm.), n^{20}D 1.211.

Anal. Calcd. for $C_{11}H_{19}O_3SiF_7$: C, 36.70; H, 5.29; F, 36.90. Found: C, 36.83; H, 5.37; F, 36.78.

There also was obtained 18.8 g. (12.3%) of tetrasubstituted silane and 111.8 g. of recovered ethyl silicate.[1]

Bis-(3,3,4,4,5,5,5-heptafluoropentyl)-diethoxysilane.—One hundred and twenty-five milliliters (0.45 N, 0.0565 mole) of 3,3,4,4,5,5,5-heptafluoropentylmagnesium bromide solution was added dropwise over three hours to 103 g. (0.29 mole) of 3,3,4,4,5,5,5-heptafluoropentyltriethoxysilane maintained at 95–105°. A white solid separated as the ether was stripped through an 18" glass helices-packed fractionating column. Pentane (500 ml.) was added to precipitate the solid, the solution was filtered, and the liquid

(2) Microanalyses were done by Mrs. C. S. Yeh, Purdue University, and the Clark Microanalytical Laboratory, Urbana, Ill.

(3) W. Simpson, British Patent 635,726 (1950).

(4) R. R. McGregor and E. L. Warrick, U. S. Patent 2,380,057 (1945).