

carbitol, 5 cc. of 28% potassium hydroxide, 3 g. of potassium iodide and 0.025 mole of the organic chlorine compound were added in the order given, shaking after each addition. The mixture was heated for the length of time indicated in the table. The alkyl 2,4-dinitrophenyl sulfide was isolated and purified as described in (A).

Alkyl 2,4-Dinitrophenyl Sulfones.—The alkyl 2,4-dinitrophenyl sulfides were converted to the corresponding sulfones by the permanganate method of Bost, Turner and Norton.⁶

(6) Bost, Turner and Norton, *THIS JOURNAL*, **54**, 1985 (1932).

CHAPEL HILL, N. C.

RECEIVED NOVEMBER 4, 1950

[CONTRIBUTION FROM NAUGATUCK CHEMICAL DIVISION OF UNITED STATES RUBBER CO.]

The Preparation of 2-Vinylthiazoles

By D. L. SCHOENE

A general method for the preparation of a series of polymerizable, new 2-vinylthiazoles has been developed. The procedure involves the condensation of α -chloroaldehydes and ketones with α -benzoxythiopropionamide to give the corresponding 2-(α -benzoxyethyl)-thiazoles which are pyrolyzed to yield the vinyl compounds. A 2-isopropenylthiazole was also prepared by an analogous synthesis.

In spite of the current interest in polymerizable vinyl compounds and the ease of synthesis of the thiazole ring, no record has been found of the preparation of 2-vinylthiazoles.¹

A practical process for the synthesis of these compounds has now been developed. A series of 2-(α -benzoxyethyl)-thiazoles was prepared by the general method of Olin and Johnson² and these, or the corresponding alcohols,³ on pyrolysis gave the desired 2-vinylthiazoles. Pyrolysis was accomplished at atmospheric pressure by dropping the liquid benzoates or alcohols through a vertical Pyrex tube filled with alumina and heated to 400–550°. Yields of 75% were obtained in the better runs.

A synthesis of 2-isopropenyl-4-methylthiazole was also accomplished using similar reactions. In this case the condensation between α -benzoxy- α -methyl thiopropionamide and chloroacetone yielded directly 25% of the isopropenylthiazole together with 48% of the expected benzoxyisopropylthiazole, subsequent pyrolysis of which proceeded smoothly.

The unsaturated thiazoles were characterized by copolymerizing them with butadiene.⁵ A homopolymer of 4-methyl-2-vinylthiazole was also prepared.

Experimental

2-(α -Benzoxyethyl)-thiazoles.—These compounds were prepared according to the general procedure of Olin and Johnson² by adding the appropriate chloroaldehyde or ketone to a benzene solution of α -benzoxythiopropionamide.⁶ The reactions were exothermic and slow additions were required for the larger runs. After two hours of reflux, dilute sodium hydroxide was added to neutrality and the organic layer was distilled. Crude yields were nearly quantitative. Yields of distilled products and physical constants are given in Table I.

In the initial work with chloroacetal and chloroacetalde-

(1) Regarding unsaturated thiazoles see: (a) E. R. Buchman and E. M. Richardson, *THIS JOURNAL*, **67**, 895 (1945); (b) G. B. Bachman and L. V. Heisey, *ibid.*, **71**, 1985 (1949); (c) H. Erlenmeyer, *et al.*, *Helv. Chim. Acta*, **31**, 1142 (1948).

(2) J. F. Olin and T. B. Johnson, *THIS JOURNAL*, **53**, 1473 (1931). See also reference (1c).

(3) Olin and Johnson² attempted without success the dehydration of 2-(α -hydroxyethyl)-4-phenylthiazole using phosphorus pentoxide in benzene.

(4) Recent work has indicated that reduced pressure will permit the use of lower temperatures with more satisfactory results.

(5) D. L. Schoene, U. S. Patent 2,515,318 (1950).

(6) J. F. Olin and T. B. Johnson, *Rec. trav. chim.*, **50**, 72 (1931).

hyde monohydrate, 95% ethanol was used as the solvent in accordance with the procedure of the original investigators. Reaction appeared complete but the products were resinous and could not be distilled without decomposition. The substitution of benzene as the solvent reduced tar formation and was used throughout this work with satisfactory results. Since this work was completed, Erlenmeyer^{1c} has reported an 86% yield using chloroacetaldehyde with absolute ethanol as the solvent. His product had a broad distillation range.

2-Vinylthiazoles.—(A) A 20-mm. o.d. Pyrex tube was packed to a depth of 20 cm. with 4–8 mesh activated alumina and supported vertically in an electrically heated furnace. The temperature was measured by a thermocouple held against the outer surface of the tube; the temperature in the reaction area undoubtedly was somewhat lower. A slow stream of nitrogen was passed through the tube while the liquid benzoates were added at the rate of 60–75 drops per minute. The pyrolysates were condensed in an ice-cooled receiver containing 1 g. of phenyl- β -naphthylamine. Initial pyrolysates were colorless but often darkened due to carbonization as the runs progressed. The products were dissolved in ether, extracted with alkali, dried over potassium carbonate and vacuum-distilled through a short packed column.

Tight packing of the pyrolysis tube was found to be responsible for most of the carbonization losses. When carbonization was severe, the purity of the distilled product, as well as yield, suffered. Essential data and yields, based on the amount of ester consumed, are given in Table II.

(B) Pyrolysis of 2-(α -benzoxyethyl)-4-methylthiazole and the parent alcohol were also accomplished by distilling from fused potassium bisulfate according to the procedure of Brooks.⁷ Two grams of potassium bisulfate and 74 g. of the alcohol gave a 19% yield of the vinylthiazole, while 30 g. each of the benzoate and potassium bisulfate gave a 49% yield. A high proportion of non-distillable residue makes the method of less interest than the alumina process.

2-Isopropenyl-4-methylthiazole.— α -Benzoxy- α -methylthiopropionamide was obtained in 82% yield as a white crystalline solid on adding⁶ hydrogen sulfide to the benzoate of acetone cyanohydrin, m.p. 41.5°; b.p. 105–111° (1 mm.) (lit.,⁸ m.p. 35–36°, 36–37°). To a solution of 382 g. (1.7 moles) of this thioamide in benzene was added 160 g. (1.73 moles) of chloroacetone. After two hours of reflux the product was distilled, yielding 59 g. (25%) of 2-isopropenyl-4-methylthiazole, b.p. 41–45° (1 mm.), n_D^{20} 1.5395, as well as 210 g. (48%) of the expected 2-(α -benzoxyisopropyl)-4-methylthiazole, b.p. 110–130° (1 mm.).

Anal. Calcd. for C_7H_9NS : S, 23.02. Found: S, 22.80.

A 200-g. portion of the ester was pyrolyzed at 500° yielding 46 g. (43%) of 2-isopropenyl-4-methylthiazole, b.p. 41–45° (1 mm.), n_D^{20} 1.5345.

Anal. Calcd. for C_7H_9NS : S, 23.02. Found: S, 21.41.

The product formed by pyrolysis, although of the same boiling range, was less pure than that formed during the condensation.

(7) L. A. Brooks, *THIS JOURNAL*, **66**, 1295 (1944).

(8) Beilstein First Supplement to Fourth Edition, Vol. IX, p. 89.

TABLE I
 2-(α -BENZOXYETHYL)-THIAZOLES

Substituent	Reactant	Yield, %	n_D^{20} , °C.	B.p. Mm.	Formula	Sulfur, % Calcd.	% Found
None	Chloroacetaldehyde monohydrate ^a	38	137-142	2	C ₁₂ H ₁₁ O ₂ NS		
4-Methyl ^b	Chloroacetone	75	155	4	C ₁₃ H ₁₃ O ₂ NS	12.96	12.69
4,5-Dimethyl ^c	3-Chlorobutanone-2 ^d	70	148	1	C ₁₄ H ₁₅ O ₂ NS	12.28	12.23
4-Phenyl ^e	Phenacyl chloride	80	194	1	C ₁₈ H ₁₅ O ₂ NS	10.35	10.09

^a Chloroacetal gave an identical yield. ^b n_D^{20} 1.5568, N calcd. 5.67, found 5.44. ^c n_D^{20} 1.5551. ^d Prepared by procedure of M. O. Forster and H. E. Furz, *J. Chem. Soc.*, 93, 675 (1908). The ketone was but once distilled and contained an undetermined amount of 1-chlorobutanone-2 which would yield the 5-ethylthiazole. ^e n_D^{20} 1.6109, Olin and Johnson³ reported a 45% yield using phenacyl bromide with alcohol as the solvent.

TABLE II

2-VINYLTIAZOLES

Substituent	Pyrolysis temp., °C.	Yield, %	n_D^{20} , °C.	B.p. Mm.	n_D^{20}	t , °C.	Formula	Sulfur, % Calcd.	% Found
None	470	59 ^a	46-47	1	1.5435	30	C ₆ H ₅ NS	28.83	27.66
4-Methyl-	500-540	72 ^b	52	8	1.5444	28	C ₆ H ₇ NS	25.60	25.22
4,5-Dimethyl ^c	400-480	38 ^d	46	4	1.5172	30	C ₇ H ₉ NS	23.02	20.74
4-Phenyl-	470	^e	100-110	1			C ₁₁ H ₉ NS		

^a 150-g. run, 70% conversion. ^b 200-g. run, 84% conversion, 9% loss in pyrolysis tube. ^c Contained some 5-ethyl-2-vinylthiazole. See Table I, note (d). ^d 70-g. run. Severe carbonization. ^e Severe carbonization losses were experienced and only 23 g. of impure product was obtained from a 138-g. run. Crude product inhibited polymerization of butadiene but was recovered in 50% yield by steam distillation from polymerization mix. Steam-distilled product copolymerized readily with butadiene and presumably was the desired compound.

Polymerization.—Details of the polymerization behavior of these unsaturated thiazoles have been reported elsewhere.⁶ It suffices to state here that the present samples all copolymerized with butadiene in a GR-S type recipe. Polymerization rates were roughly proportional to purity with the

better samples copolymerizing faster than styrene in the same recipe. A solid homopolymer of 4-methyl-2-vinylthiazole was also prepared in emulsion.

NAUGATUCK, CONN.

RECEIVED AUGUST 28, 1950

[CONTRIBUTION NO. 799 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Propargylic Rearrangement. III. Allenic Acids from Secondary and Tertiary Propargylic Bromides

BY JOHN H. WOTIZ AND ROBERT J. PALCHAK¹

A secondary and a tertiary propargylic bromide have been converted into allenic acids by carbonation of their Grignard reagents. The unsymmetrical allene, 2,3-octadiene-4-carboxylic acid, has been resolved through its strychnine salt.

In a recent publication² it was shown that carbonation of a Grignard reagent from a primary propargylic bromide yields a mixture of an acetylenic, allenic and an unidentified dimeric acid. The present study was undertaken in order to prepare and investigate the allenic acids by carbonation of the Grignard reagents from secondary and tertiary propargylic bromides.

The secondary and tertiary propargylic bromides used in this study were 2-bromo-3-octyne (I), C₄H₉-C≡C-CHBr-CH₃ and 2-bromo-2-methyl-3-octyne (II), C₄H₉-C≡C-CBr(CH₃)₂. They were converted into Grignard reagents using the cyclic reactor which allows the preparation of Grignard reagents from very active halides.³ On carbonation and hydrolysis,² the secondary bromide (I) yielded 45% of an acidic material, at least 20% of which is 2,3-octadiene-4-carboxylic acid (III), C₄H₉-C(CO₂H)=C=CH-CH₃. Its infrared spectrum⁴ showed the presence of a strong

band near 1950 cm.⁻¹, characteristic for compounds containing the allenic linkage, and the absence of an acetylenic bond absorption band. The theoretical amount of hydrogen was quickly absorbed on hydrogenation at pressures slightly above atmospheric, using Adams catalyst. The hydrogenated acid was converted into its amide which did not depress the melting point of an authentic sample of α -propylhexanamide. Fractionation of the mother liquor afforded a liquid acid, C₆H₁₄O₂, which absorbed the theoretical amount of hydrogen (2 moles). The amide of the corresponding saturated acid did not depress the melting point of the amide of α -methyloctanoic acid. However, the original acid was not homogeneous, as shown by its infrared spectrum which exhibited a band of medium intensity at 1950 cm.⁻¹ (allenic group) and a very weak band at 2240 cm.⁻¹ (acetylenic group).⁵ Purification by the chromatographic method of Marvel and Rands⁵ was unsuccessful. Ozonization yielded unidentified fragments.

The Grignard reagent from the tertiary bromide

(1) Abstracted from the thesis of R. J. Palchak presented in partial fulfillment of the requirements for the degree of Master of Science.

(2) J. H. Wotiz, *THIS JOURNAL*, **72**, 1639 (1950).

(3) D. C. Rowlands, K. W. Greenlee and C. E. Boord, Abstracts of the 117th A. C. S. Meeting, Philadelphia, April, 1950.

(4) Infrared analyses by Dr. F. A. Miller and co-workers at the Mellon Institute, Pittsburgh, Pa.

(5) The weakness of this band is in line with previous observations: J. H. Wotiz and F. A. Miller, *THIS JOURNAL*, **71**, 3441 (1949).

(6) C. S. Marvel and R. D. Rands, *ibid.*, **72**, 2642 (1950).