TABLE I

2-(α-BENZOXYETHYL)-THIAZOLES

Substituent	Reactant	Yield, %	B.p. °C.	B.p. Mm.	Formula	Sulfur, % Calcd.	Sulfur, % Found
None	Chloroacetaldehyde monohydrate[a]	38	137–142	2	$C_{12}H_{11}O_2NS$		
4-Methyl[b]	Chloroacetone	75	155	4	$C_{13}H_{13}O_2NS$	12.96	12.69
4,5-Dimethyl[c]	3-Chlorobutanone-2[d]	70	148	1	$C_{14}H_{15}O_2NS$	12.28	12.23
4-Phenyl[e]	Phenacyl chloride	80	194	1	$C_{18}H_{15}O_2NS$	10.35	10.09

[a] Chloroacetal gave an identical yield. [b] $n^{26}D$ 1.5568, N calcd. 5.67, found 5.44. [c] $n^{20}D$ 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] $n^{26}D$ 1.6109, Olin and Johnson[3] reported a 45% yield using phenacyl bromide with alcohol as the solvent.

TABLE II

2-VINYLTHIAZOLES

Substituent	Pyrolysis temp., °C.	Yield, %	B.p. °C.	B.p. Mm.	n_D	t, °C.	Formula	Sulfur, % Calcd.	Sulfur, % Found
None	470	59[a]	46–47	1	1.5435	30	C_5H_5NS	28.83	27.66
4-Methyl-	500–540	72[b]	52	8	1.5444	28	C_6H_7NS	25.60	25.22
4,5-Dimethyl[c]	400–480	38[d]	46	4	1.5172	30	C_7H_9NS	23.02	20.74
4-Phenyl-	470	[e]	100–110	1			$C_{11}H_9NS$		

[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.

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[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. PALCHAK[1]

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 publication[2] 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), $C_4H_9—C{\equiv}C—CHBr—CH_3$ and 2-bromo-2-methyl-3-octyne (II), $C_4H_9—C{\equiv}C—CBr(CH_3)_2$. 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), $C_4H_9—C(CO_2H){=}C{=}CH—CH_3$. Its infrared spectrum[4] 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, $C_6H_{14}O_2$, 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 Rands[6] was unsuccessful. Ozonization yielded unidentified fragments.

The Grignard reagent from the tertiary bromide

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(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).

II gave on carbonation solid 2,3-octadiene-2-methyl-4-carboxylic acid, $C_4H_9{-}C(CO_2H){=}C{=}C(CH_3)_2$ in a 9% yield. The intensity of its allenic absorption band was about the same as that of III. The absence of the isomeric acetylenic acid may be due to a steric effect. The Grignard reagent of the allenic form, $R{-}C(MgBr){=}C{=}CR_2$, is much less sterically hindered than the acetylenic isomer, $R{-}C{\equiv}C{-}CR_2{-}MgBr$.

No direct resolution of an allenic compound has been reported, although Maitland and Mills[7] accomplished the asymetric synthesis of an optically active allenic hydrocarbon and Kohler, *et al.*,[8] resolved an allenic acid by the crystallization of the brucine salt of its glycolic acid ester. 2,3-Octadiene-4-carboxylic acid possesses molecular asymmetry, and we have been able to effect a direct resolution of it. Of six optically active alkaloids tested, strychnine appeared to give the most suitable salt with this acid, and an acid–base ratio of approximately 2:1 was used as suggested by Ingersoll.[9] Fractional crystallization from mixtures of ethyl acetate and chloroform was carried out until the salt (1:1) had a constant melting point and a constant specific rotation $[\alpha]^{25}\text{D}$ −72.69° in chloroform. Decomposition of the salt was brought about by heating with ether, or by stirring with a mixture of dilute hydrochloric acid and ether. The latter procedure gave a purer product. The resolved acid was recrystallized from petroleum ether to a constant melting point of 49–50° and a specific rotation of $[\alpha]^{25}\text{D}$ −30.69° in chloroform.

Experimental[10]

The preparation and the physical properties of the propargylic alcohols and bromides were included in a recent publication dealing with their infrared spectra.[11]

The allenic acids were formed and characterized using the experimental procedures described for the acids from primary propargylic bromides.[2] A solution of 50.0 g. (0.265 mole) of 2-bromo-3-octyne (I), (b.p. 43° at 1 mm., $n^{25}\text{D}$ 1.4805) in 250 cc. of ether yielded 17.0 g. (41.6% yield) of acidic material which on two recrystallizations from petroleum ether (30–60°) yielded 3.4 g. (20% of the acidic mixture) of **2,3-octadiene-4-carboxylic acid, II**; m.p. 59–60°, b.p. 105° at 2 mm. neut. equiv. 155 (theory is 154). *Anal.* Calcd. for $C_9H_{14}O_2$: C, 70.1; H, 9.1. Found: C, 70.0; H, 9.0. A sample of this acid (0.6807 g., 0.0044 mole) absorbed 215 cc. (S.T.P.) of hydrogen (99.9%) in 340 minutes.

Similarly, 56.0 g. (0.276 mole) of 2-bromo-2-methyl-3-octyne, II (b.p. 52° at 1 mm., $n^{25}\text{D}$ 1.4755) yielded 4.4 g. (9.5% yield) of solid **2,3-octadiene-2-methyl-4-carboxylic acid**, m.p. 77–78°, neut. equiv. 169 (theory is 168). *Anal.* Calcd. for $C_{10}H_{16}O_2$: C, 71.5; H, 9.5. Found: C, 71.3; H, 9.3. In the hydrogenation of 0.1616 g. (0.000868 mole) of this acid, 38 cc. (S.T.P.) of hydrogen (99.9%) was absorbed in 50 minutes.

α-Propylhexanoic acid was prepared by the malonic ester synthesis[12]; b.p. 97° at 1 mm., $n^{25}\text{D}$ 1.4268. *Anal.* Calcd. for $C_9H_{18}O_2$: C, 68.4; H, 11.4. Found: C, 68.4; H, 11.4. It was converted into **α-propylhexanamide**; m.p. 112° from petroleum ether (30–60°). *Anal.* Calcd. for $C_9H_{19}ON$: C, 68.7; H, 12.2. Found: C, 68.5; H, 11.9. Similarly was prepared **α-isobutylhexanoic acid**; b.p. 241°, $n^{25}\text{D}$ 1.4289. *Anal.* Calcd. for $C_{10}H_{20}O_2$: C, 69.8; H, 11.6. Found: C, 69.6; H, 11.3. It was converted into **α-isobutylhexanamide**; m.p. 103–104° from petroleum ether (30–60°). *Anal.* Calcd. for $C_{10}H_{21}ON$: C, 70.0; H, 12.3; N, 8.2. Found: C, 70.1; H, 12.0; N, 8.0.

An authentic sample of **α-methyloctanoic acid** was prepared by the carbonation of the Grignard reagent from 2-bromooöctane; b.p. 103° at 2 mm., $n^{25}\text{D}$ 1.4274. *Anal.* Calcd. for $C_9H_{18}O_2$: C, 68.4; H, 11.4. Found: C, 68.2; H, 11.5. It was converted into its amide which when recrystallized from petroleum ether (30–60°) melted at 79–80°.[13]

Distillation of the Mother Liquor from III.—A 13.5-g. sample distilled at 125° at 2 to 1 mm. yielding 7.0 g. of a colored distillate; neut. equiv., 162. This was combined with 21 g. of distillate obtained previously, extracted with alkali and reprecipitated with hydrochloric acid. Its ether solution was dried with sodium sulfate and redistillation yielded 17 g. of a colorless liquid; b.p. 110° at 2 mm., neut. equiv., 157. *Anal.* Calcd. for $C_9H_{14}O_2$: C, 70.1; H, 9.1. Found: C, 69.8; H, 8.8. Its infrared spectrum showed the presence of a weak triple bond band and a medium strong allenic bond absorption band. In the hydrogenation of a 1.3726-g. sample (0.0089 mole for $C_9H_{14}O_2$), 391 cc. (S.T.P.) of hydrogen (98% of theory) was absorbed in 90 minutes. The saturated acid was converted into its amide which melted at 79–80° and did not depress the melting point of an authentic sample of α-methyloctanamide.

The Resolution of 2,3-Octadien-4-carboxylic Acid into Its Optically Active Components.—All optical measurements were made on a Bausch and Lomb saccharimeter in chloroform solutions using a two decimeter tube. A chloroform solution of 2.1735 g. (0.0065 mole) of strychnine and 1.9225 g. (0.0125 mole) of III, after standing for 12 hours, was evaporated to a thick sirup, 5 cc. of ethyl acetate was added causing a white precipitate to form. Six recrystallizations from a mixture of chloroform and ethyl acetate gave a white solid, m.p. 126–127°,[14] $[\alpha]^{25}\text{D}$ −72.69°. *Anal.* Calcd. for $C_{30}H_{36}N_2O_4$: C, 73.8; H, 7.4; N, 5.9. Found: C, 73.8; H, 7.3. N, 5.6.

Decomposition of the Salt with Solvent.—A small portion of the salt was dissolved in chloroform and allowed slowly to evaporate until crystals were formed. The remaining solvent was then removed under vacuum. The residue was extracted with ether, and the ether soluble material crystallized from petroleum ether (30–60°) to a melting point of 46–47°.

Decomposition of the Salt with Acid.—The salt was stirred with a mixture of dilute hydrochloric acid and ether. The aqueous layer was washed with three portions of ether, all the ether layers were combined and the ether soluble material crystallized from petroleum ether (30–60°) to a maximum constant melting point of 49–50° and a rotation of $[\alpha]^{25}\text{D}$ −30.69°. *Anal.* Calcd. for $C_9H_{14}O_2$: C, 70.3; H, 9.1. Found: C, 70.2; H, 9.1.

PITTSBURGH, PENNA. RECEIVED OCTOBER 12, 1950

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[7] P. Maitland and W. H. Mills, *Nature*, **135**, 994 (1935).

[8] E. P. Kohler, J. T. Walker and M. Tishler, THIS JOURNAL, **57**, 1743 (1935).

[9] A. W. Ingersoll, *ibid.*, **47**, 1168 (1925).

[10] Microanalyses by the Microanalytical Laboratory of the University of Pittsburgh.

[11] J. H. Wotiz, F. A. Miller and R. J. Palchak, THIS JOURNAL, **72**, 1639 (1950).

[12] Supplied by M. J. F. Hedenburg, Mellon Institute, Pittsburgh, Pa.

[13] D. S. Tarbell and M. Weiss, THIS JOURNAL, **61**, 1203 (1939), report the melting point of 79–80°.

[14] After collapsing at 126–127°, there remains a mixture of liquid melt and solid up to the point where the solid begins to turn dark, usually about 140°.