Twenty milliliters of this filtered solution was mixed with 20 ml. of a filtered solution containing the compound (1 gram dissolved in 100 ml. of absolute ethanol). The mixtures were chilled to give Burgundy red colored crystals. The compounds were recrystallized once from ethanol: I_A, m.p. 148° C. (decomposed); Anal. calcd. $C_{16}H_{13}N_5O_7$: N, 18.05; Found: N, 17.88; III_A, m.p. 183° C. (decomposed); Anal. calcd. $C_{17}H_{15}N_5O_7$: N, 17.45; Found: N, 17.70.

Compound VI. When 0.1 mole of 3-(*N,N*-dimethylamino) phenol was mixed with 0.1 mole of ethyl acetoacetate and treated under the same conditions used to prepare the I to V series, a 65% yield of 7-(dimethylamino)-4-methyl coumarin was obtained. The compound was purified by taking up the substance in the ethyl acetate and precipitating the material with heptane. The process was repeated twice additionally, m.p. 139.5° C. [lit. 144° C. (*1*)]. Dilute solutions of hydrochloric acid dissolve the compound to give a reddish solution.

Compound VII. A mixture of 0.1 mole of *m*-amino phenol and 0.1 mole of ethyl acetoacetate was treated under the same conditions use to prepare the I to V series. The compound was purified by taking it up in tetrahydrofuran and then precipitating it with heptane. The process was repeated for a second recrystallization, yield 96%, m.p. >300° C.

Dilute hydrochloric acid solutions show no effect on the compound and indicate that the amino group of *m*-phenol is now the substituted amide group of 7-hydroxy-4-methylcarbostyril. Anal. calcd. $C_{10}H_9NO_2$: C, 68.55; H, 4.67; N, 7.99; Found: C, 68.37; H, 4.49; N, 8.22.

ACKNOWLEDGMENT

The analyses were performed by Carl Tiedcke, Teaneck, N. J., and the PMR spectrum was made and interpreted by Sadtler Research Laboratories, Philadelphia, Pa.

LITERATURE CITED

(1) Dey, B.B., *J. Chem. Soc.* **1915**, pp. 107, 1644.
(2) Rodd, E.H., "Chemistry of Carbon Compounds," **III B**, p. 1000, Elsevier Press, New York, 1956.
(3) Wheelock, C.E., *J. Am. Chem. Soc.* **81**, 1348 (1959).
(4) Woods, L.L., Sapp, John, *J. Org. Chem.* **27**, 3703 (1962).

RECEIVED for review October 10, 1967. Accepted February 28, 1968. The authors thank the Robert A. Welch Foundation for financial assistance.

Aziridine Adducts of α, β-Unsaturated Nitriles

LEON H. CHANCE, DONALD J. DAIGLE, and GEORGE L. DRAKE, Jr.
Southern Regional Research Laboratory, New Orleans, La. 70119

The aziridine adducts of crotononitrile, 2-methyleneglutaronitrile, cinnamonitrile, and methacrylonitrile were prepared. The products obtained were 3-(1-aziridinyl)butyronitrile, 2-(1-aziridinylmethyl)glutaronitrile, 3-(1-aziridinyl)3-phenylpropionitrile, and 3-(1-aziridinyl)2-methyl propionitrile, respectively. Aziridine also reacted with allyl cyanide, yielding a product identical with the aziridine adduct of crotononitrile. Apparently, allyl cyanide rearranges to crotonitrile in the presence of aziridine, and then aziridine adds to the crotonitrile. All of the adducts polymerized readily in aqueous media in the presence of zinc fluoborate.

THE reaction of aziridine with acrylonitrile, acrylamide, methyl acrylate, crotonamide, and methyl crotonate were reported by Bestian (*3*). In some of these reactions, either sodium methylate or metallic sodium was employed as the catalyst. Yoshida and Naito reported that in this type of reaction the aziridine group added to the β-carbon of the double bond to form the aziridine adducts (*5*).

The present authors prepared the adducts of aziridine (I) and crotononitrile (II), 2-methylene glutaronitrile-(acrylonitrile dimer) (III), cinnamonitrile (IV), and methacrylonitrile (V). The products obtained were 3-(1-aziridinyl)butyronitrile (VI), 2-(1-aziridinylmethyl)glutaronitrile (VII), 3-(1-aziridinyl)-3-phenylpropionitrile (VIII), and 3-(1-aziridinyl)-2-methylpropionitrile (IX), respectively. VI and VII required only heat to complete the reaction, whereas VIII and IX required heating in the presence of catalytic amounts of metallic sodium. The reaction of aziridine with allyl cyanide was also tried. The product obtained had the same boiling point, infrared spectrum, and refractive index as that obtained from the reaction of aziridine with crotononitrile. Apparently, allyl cyanide rearranges to crotononitrile in the presence of the aziridine (a base), and then aziridine adds to the crotononitrile to give the identical compound. The rearrangement of allyl cyanide to crotononitrile in the presence of alkali is well known (*1*).

Infrared spectra of VI, VII, VIII, and IX showed the typical absorption band for C≡N at 2257 to 2262 cm.$^{-1}$. All four compounds had sharp, intense bands in the region 1259 to 1274 cm.$^{-1}$, characteristic of the aziridine ring (*4*). The cinnamonitrile adduct had bands at 1605 and 1590 cm.$^{-1}$ and also at 756 and 698 cm.$^{-1}$, attributed to the benzene ring.

The polymerization of some *N*-substituted aziridines has been studied by Barb (*2*). Compounds VI, VII, VIII, and IX polymerized in aqueous solutions in the presence of $Zn(BF_4)_2$. In all cases, water insoluble polymers formed rapidly at room temperature.

EXPERIMENTAL

3-(1-Aziridinyl)butyronitrile (VI). Compound I (50.0 grams, 1.16 moles) was added dropwise with stirring to a flask containing II (67.0 grams, 1.0 mole). There was no temperature change. The solution was heated at reflux for 9 hours and the product distilled, yielding 53.7 grams

(48.8%) of VI, a colorless water soluble liquid, b.p. 194.5–5.5° C./765 mm., n_D^{30} 1.43979. Anal. Calcd. for $C_6H_{10}N_2$: C, 65.41; H, 9.15; N, 25.43. Found: C, 65.37; H, 9.15; N, 25.44.

Reaction of Allyl Cyanide and Aziridine. Allyl cyanide (109.8 grams, 1.64 moles) and aziridine (70.5 grams, 1.64 moles) were placed in a flask and allowed to stand overnight. After the solution was heated on a steam bath for 6 hours, the product was vacuum distilled, yielding a fraction, of 62 grams, b.p. up to 76° C./10 mm.; a second fraction of 64.4 grams (35.7%), b.p. 76–7° C./10 mm.; and a viscous residue. The second fraction was redistilled to yield a product identical to VI, b.p. 193–4° C./760 mm., n_D^{30} 1.43980. The infrared spectrum was identical to that of VI.

2-(1-Aziridinylmethyl)glutaronitrile (VII). Compounds I (30.0 grams, 0.7 mole) and III (53.0 grams, 0.5 mole) were mixed in a flask and heated on a water bath at 80° C. for 9.5 hours. The product was distilled, yielding 66 grams (88.6%) of VII, a colorless water soluble liquid, b.p. 103–4° C./0.07 mm. Anal. Calcd. for $C_8H_{11}N_3$: C, 64.41; H, 7.43; N, 28.17. Found: C, 64.60; H, 7.60; N, 28.04.

3-(1-Aziridinyl)-3-phenylpropionitrile (VIII). Compounds I (12.9 grams, 0.3 mole) and IV (25.6 grams, 0.198 mole) were placed in a flask and heated on a water bath at 70° C. for 7 hours. The aziridine was recovered unreacted. Fresh aziridine (15 grams) was added to unchanged IV, and 0.4 gram of metallic sodium was added. The mixture was heated under a blanket of nitrogen gas for 1.25 hours at 65° C. After standing for 48 hours, 10 grams more of I and 0.1 gram of fresh sodium were added, and heating resumed for 2 hours at 70° C. The dark brown mixture was distilled, yielding 21.5 grams (63.0%) of VIII, a colorless water insoluble oil, b.p. 91° C./0.03 mm. The oil was redistilled for analysis. Anal. Calcd. for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02; N, 16.27; mol. wt., 172.2. Found: C, 76.88; H, 6.99; N, 16.34; mol. wt., 170. (Osmometer method).

3-(1-Aziridinyl)-2-methylpropionitrile (IX). Compounds I (53.0 grams, 1.23 moles), V (67.1 grams, 1.0 mole), and 0.5 gram of metallic sodium were placed in a flask and heated under reflux in a water bath at 60° C. for about 16 hours. After the first hour of heating, 10 ml. of fresh aziridine was added, and after 8 hours, an additional 10 ml. was added. The mixture turned a dark brown and upon distillation yielded 41 grams (41%) of IX, a colorless water soluble liquid, b.p. 68–70° C./11 mm. Anal. Calcd. for $C_6H_{10}N_2$: C, 65.41; H, 9.15; N, 25.43. Found: C, 65.30; H, 9.21; N, 25.44.

ACKNOWLEDGMENT

The authors thank Nancy M. Morris and Elizabeth R. McCall for the infrared analyses.

LITERATURE CITED

(1) Auwers, K.V., *Ber.* **56B**, 1172 (1923).
(2) Barb, W.G., *J. Chem. Soc.* **1955**, p. 2577.
(3) Bestian, H., *Ann. Chem.* **566**, 210 (1950).
(4) Spell, H.L., *Anal. Chem.* **39** (2), 185 (1967).
(5) Yoshida, T., Naito, K., *J. Chem. Soc. Japan, Ind. Chem. Sect.* **55**, 455 (1952); *CA* **48**, 13625*g* (1954).

RECEIVED for review October 18, 1967. Accepted December 19, 1967. The Southern Regional Research Laboratory is one of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

New Procedure for the Preparation of Pure Optical Isomers of 2-Amino-5-phenyl-2-oxazolin-4-one

MICHAEL R. HARNDEN
Organic Chemistry Department, Research Division, Abbott Laboratories, North Chicago, Ill. 60064

Separation of diastereomeric 2-octyl mandelates by vapor-phase chromatography and reaction of the esters with guanidine provide a convenient economical route to enantiomers of 2-amino-5-phenyl-2-oxazolin-4-one.

THE central nervous system stimulating properties of 2-amino-5-phenyl-2-oxazolin-4-one (pemoline) have been described previously (*1*, *2*). There is also evidence that pemoline accelerates acquisition and enhances retention of a conditioned avoidance response in experimental animals (*3*). The enantiomers of pemoline have previously been prepared by reaction of guanidine with the enantiomers of methyl mandelate and only the D(+) isomer was reported to possess biological activity (*4*). Therefore, the author was interested in investigating more economical alternative routes to optically active pemoline.

Racemic mandelic acid was esterified with L-2-octanol and the diastereomeric esters separated using vapor-phase chromatography and identified by comparison with samples obtained from D- and L-mandelic acid. Reaction of each diastereomer with guanidine yielded optically active pemoline in yields comparable with those from methyl mandelate (*4*).

Resolution of organic compounds is generally a relatively expensive operation. In the procedure (*4*) previously described, the optically active mandelic acid is completely utilized, whereas in the procedure described above, racemic mandelic acid is used and the optically active 2-octanol can be readily recovered and recycled. Either enantiomer of 2-octanol could obviously be used.

EXPERIMENTAL

Melting points were measured on a Thomas-Hoover capillary melting point apparatus and are corrected. Optical rotations were determined with a Hilger-Watts polarimeter using 0.5% solutions in dimethylformamide for 2-amino-5-phenyl-2-oxazolin-4-one samples and 1% solutions in acetone for all other samples.

Preparation of L-2-Octyl-DL-mandelate. DL-Mandelic acid (22.8 grams, 0.15 mole), L-2-octanol (19.5 grams, 0.15 mole,