reaction reported to be acid catalyzed for acylated cyanoguanidines.[12] The water necessary for this hydrolysis must have been provided by the decomposition of the initially dry formic acid to CO plus H_2O. Vigorous evolution of a gas, presumably CO, was observed during the reaction, at temperatures well below the boiling point of formic acid. Since formic acid, *per se*, is stable under these conditions, one must conclude that cyanoguanidine somehow catalyzes the decomposition of formic acid. Its ability to do so, albeit at a reduced rate, was demonstrated even at room temperature.

The cyclization of guanylurea formate by heating at 150° represents a novel method for synthesizing the *s*-triazine ring. Since this reaction results in the incorporation of the carbon of formate into the *s*-triazine ring, it may provide the basis for the synthesis of several disubstituted *s*-triazines from a variety of formate salts of acylcyanoguanidines[12,13] or from other carboxylic acid salts of amidinourea.

Experimental Section

Melting points were measured on a Fisher-Johns apparatus. Ultraviolet absorption spectra were recorded with a Cary Model 15 spectrophotometer. Infrared spectra were obtained from pressed KBr disks with a Perkin-Elmer Model 337 spectrophotometer. Mass spectra were obtained on a Bendix time of flight spectrometer at a probe temperature of 105°. Paper chromatography was performed on Whatman 3 MM with *n*-butyl alcohol–methyl alcohol–water (4:1:1) as the solvent. Spots on the paper chromatograms were visualized with a spray active N–H group.[14] Elemental analyses were performed by the Galbraith Laboratories of Knoxville, Tenn.

Amidinourea Formate.—Cyanoguanidine (8.6 g) and 13.8 g of dry formic acid were heated under reflux to 80°. Heating was discontinued and the temperature of the reaction mixture was allowed to rise to 120°. An ice bath was kept at hand to control excessive rates of reaction. After 10 min the reaction subsided and the reaction mixture solidified. The solid was washed with alcohol and recrystallized twice from water: mp 140–145° (with effervescence); $\lambda_{max}^{0.1\ N\ NaOH}$ 219 mμ (ε 21,000); J = 1.5 ($HCOO^-$) and 2.0–3.0 cps (7 H) in dimethyl sulfoxide; J = 0.6 ($HCOO^-$), 1.8 (1 H), and 2.5 cps (6 H) in trifluoroacetic acid; $\bar{\nu}_{max}$ 3440, 3300, 3100 (NH, $CONH_2$), 2800, 2720 (acidic H), 1755, 1715, 1645, 1610, 1470 (COO^-, $CONH_2$, NH), 1395 (NH), 1365 (C=O), 1090, 918, 855, 770, 730, 710 cm^{-1} (NH, C=O, CN); solubility (at 25°) 0.3 g/100 ml of H_2O, 4.2 g/100 ml of DMSO. *Anal.* Calcd for $C_3H_8N_4O_3$: C, 24.32; H, 5.40; N, 37.82. Found: C, 24.43, 25.24; H, 5.40, 5.74; N, 38.45, 37.48.

Conversion of Amidinourea Sulfate to Amidinourea Formate.—The sulfate (4.0 g) was heated into solution with 20 ml water and allowed to cool to room temperature; 4.16 g of $Ba(OH)_2 \cdot 8H_2O$ was added, the precipitate was removed, and 2.0 ml of dry formic acid was added. The mixture was dried *in vacuo* at 40°. The melting point, ultraviolet, infrared, and chromatographic characteristics were identical with those given above.

Amidinourea Hydrochloride.—Amidinourea formate (740 mg, intermediate) in 200 ml of distilled water was passed through a 1 × 20 cm column of Bio-Rad AG 21K resin in the chloride form. The effluent was lyophilized and a sample was submitted without further treatment for analysis, mp 140–142° dec. *Anal.* Calcd for $C_2H_7ClN_4O$: C, 17.44; H, 5.07; Cl, 25.28; N, 40.60. Found: C, 17.86, 17.84; H, 4.99, 5.10; Cl, 24.70, 24.53; N, 40.16, 40.26.

2-Amino-4-hydroxy-*s*-triazine.—Amidinourea formate (1 g) was placed as a thin layer in a 10-cm petri dish into a preheated oven at 150° for 90 min, yielding 671 mg (81.5%): mp >300°; $\lambda_{max}^{0.01\ N\ NaOH}$ 250 mμ (ε 3300); solubility (at 25°) 0.0015 g/100 ml of H_2O.

Registry No.—I, 10043-39-7; II, 4040-10-2; amidinourea hydrochloride, 926-72-7.

(12) P. Adams, D. W. Kaiser, D. E. Nagy, G. A. Peters, R. L. Sperry, and J. T. Thurston, *J. Org. Chem.*, **17**, 1162 (1952).
(13) D. W. Kaiser and J. T. Thurston, *Chem. Abstr.*, **41**, 481 (1947).
(14) R. H. Mazur, B. W. Ellis, and P. S. Cammarata, *J. Biol. Chem.*, **237**, 1619 (1962).

Ketenes. XII. Structure of Ketene–Enamine Cycloadducts[1]

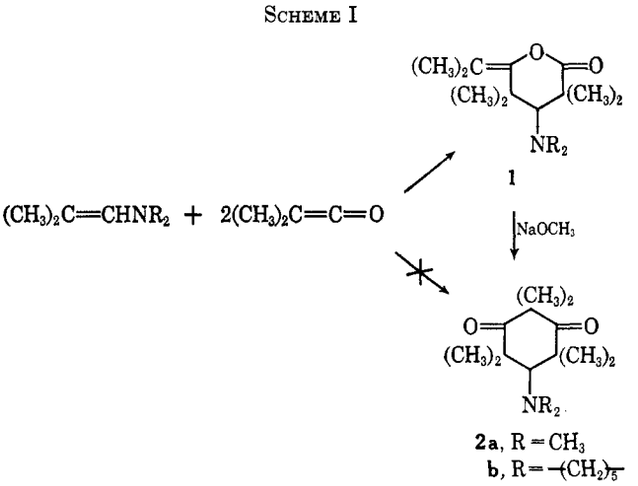
JAMES C. MARTIN,[2] PAUL G. GOTT, AND H. U. HOSTETTLER

Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee

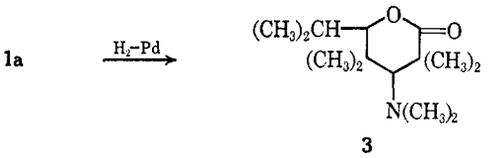
Received November 7, 1966

In an earlier publication we reported the synthesis of 2:1 cycloadducts from dimethylketene and isobutenylamines.[3] The aminocyclohexanedione structures (**2**) assigned to these products were in error; the compounds are actually enol lactones (**1**). (See Scheme I.)

SCHEME I



The correct structures were indicated by the chemical shifts for an isopropylidene group (singlets at 1.70 and 1.81 ppm which correspond to values noted in recent work on other cycloadducts of dimethylketene[4–7]). Further evidence for the presence of the isopropylidene group was obtained by catalytic hydrogenation to **1a** to the saturated δ-lactone (**3**).



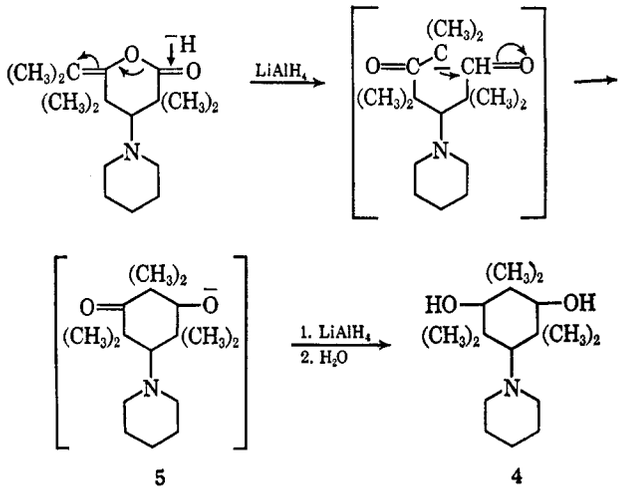
When heated with sodium methoxide, **1a** and **1b** rearranged easily, in a manner analogous to the base-catalyzed rearrangement of compounds with similar

(1) Paper XI in this series: E. U. Elam, *J. Org. Chem.*, **32**, 215 (1967).
(2) To whom all correspondence should be addressed.
(3) R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **28**, 1468 (1963).
(4) J. C. Martin, V. A. Hoyle, Jr., and K. C. Brannock, *Tetrahedron Letters*, 3589 (1965).
(5) J. C. Martin, K. C. Brannock, and R. H. Meen, *J. Org. Chem.*, **31**, 2966 (1965).
(6) H. U. Hostettler, *Tetrahedron Letters*, 1941 (1965).
(7) R. N. Pratt, S. A. Proctor, and G. A. Taylor, *Chem. Commun.*, 574 (1965).

structures,[4,5] to form the corresponding aminocyclohexanediones (**2a** and **2b**) in good yields.

In our original publication the reduction of **1b** by lithium aluminum hydride to the aminocyclohexanediol (**4**) was described. It is likely that the basic reagent caused the rearrangement of the lactone to diol **4** *via* the hydroxy ketone (**5**). Hydride reduction of dione **2b** also afforded the identical glycol **4**. An analogous rearrangement during hydride reduction has been reported.[4]

SCHEME II



5 4

Experimental Section

3-(Dimethylamino)-5-hydroxy-2,2,4,4,6-pentamethyl-5-heptenoic Acid δ-Lactone (1a).—This material was prepared as described previously.[3] Infrared spectrum (neat) showed 5.72 and 6.00 μ. Nmr spectrum[8] ($CDCl_3$) indicated singlets at 1.24 (3 H), 1.29 (3 H), and 1.35 (6 H) (methyl groups); singlets at 1.70 (3 H) and 1.81 (3 H) (isopropylidene group); a singlet at 2.55 (1 H) (methylidyne proton); and a singlet at 2.62 ppm (6 H) (dimethylamino group).

5-Hydroxy-2,2,4,4,6-pentamethyl-3-piperidino-5-heptenoic Acid δ-Lactone (1b).—This material was prepared as described previously.[3] Infrared spectrum (neat) showed 5.74 and 6.00 μ; nmr spectrum ($CDCl_3$) indicated singlets at 1.30 (6 H), 1.35 (3 H), and 1.39 (3 H) (methyl groups); a broad peak at 1.44 (6 H) (piperidine ring); singlets at 1.72 (3 H) and 1.83 (3 H) (isopropylidene group); a singlet at 2.51 (1 H) (methylidyne proton); and a broad peak at 2.86 ppm (4 H) (piperidine ring protons on carbon adjacent to nitrogen).

5-(Dimethylamino)-2,2,4,4,6,6-hexamethyl-1,3-cyclohexanedione (2a).—A solution of 20.4 g of **1a** and 2.0 g of sodium methoxide in 50 ml of toluene was heated for 16 hr on a steam bath. The mixture was washed with water and dried over anhydrous magnesium sulfate; the toluene was removed *in vacuo*. There remained 19.8 g of crude **2a**, mp 69–73°. One recrystallization from hexane gave 16.3 g (80%) of **2a**, mp 78–79°. Infrared spectrum (KBr) showed 5.79 and 5.91 μ. Nmr spectrum ($CDCl_3$) indicated singlets at 1.27 (9 H) and 1.30 (9 H) (methyl groups); a singlet at 2.70 (6 H) (dimethylamino group); and a singlet at 2.95 ppm (1 H) (methylidyne proton).

Anal. Calcd for $C_{14}H_{25}NO_2$: C, 70.2; H, 10.5; N, 5.9. Found: C, 70.2; H, 10.7; N, 5.7.

2,2,4,4,6,6-Hexamethyl-5-piperidino-1,3-cyclohexanedione (2b).—A solution of 34.7 g of **1b** and 2.0 g of sodium methoxide in 70 ml of toluene was heated for 16 hr on a steam bath. The mixture was washed with water and dried over anhydrous magnesium sulfate; the toluene was removed *in vacuo*. There remained 30.6 g (88%) of **2b**, mp 116.5–118°. A sample for analysis that was recrystallized from hexane melted at 118–118.5°. Infrared spectrum (KBr) showed 5.82 and 5.93 μ. Nmr spectrum ($CDCl_3$) indicated singlets at 1.25 (9 H) and 1.31 (9 H) (methyl groups); a broad peak at 1.52 (6 H) (piperidine ring); a singlet at 2.87 (1 H) (methylidyne proton); and a broad peak at 2.98 ppm (4 H) (piperidine ring protons on carbon adjacent to nitrogen).

Anal. Calcd for $C_{17}H_{29}NO_2$: C, 73.2; H, 10.4; N, 5.0. Found: C, 73.0; H, 10.5; N, 5.2.

3-(Dimethylamino)-5-hydroxy-2,2,4,4,6-pentamethylheptanoic Acid δ-Lactone (3).—A solution of 30 g of **1a** in 100 ml of cyclohexane was hydrogenated over 10 g of 5% palladium on alumina in a rocking autoclave for 5 hr at 130° and 1500 psi. The autoclave was cooled, and the contents were filtered to remove the catalyst. Examination of the filtrate by gas–liquid partition chromatography showed the presence of about 15% unchanged **1a**. Distillation through a Nestor–Faust spinning-band column gave some impure product together with 17.2 g of **3**, bp 106° (0.6 mm). This material solidified on standing, and a sample recrystallized from hexane melted at 54–56°. Infrared spectrum (KBr) showed 5.83 μ. Nmr spectrum ($CDCl_3$) indicated a pair of doublets at 0.99 and 1.04 (6 H) and multiplet at 2.01 (1 H) (isopropyl group); singlets at 1.08 (3 H), 1.12 (3 H), 1.30 (3 H), and 1.33 (3 H) (methyl groups); a singlet at 2.53 (1 H) (methylidyne proton on carbon bearing dimethylamino group); a singlet at 2.64 (6 H) (dimethylamino group); and a doublet at 3.71 ppm (1 H) (methylidyne proton).

Anal. Calcd for $C_{14}H_{27}NO_2$: C, 69.7; H, 11.3; N, 5.8. Found: C, 69.6; H, 11.5; N, 5.9.

2,2,4,4,6,6-Hexamethyl-5-piperidino-1,3-cyclohexanediol (4).—To a stirred suspension of 3.04 g (0.08 mole) of lithium aluminum hydride in 100 ml of tetrahydrofuran was added over a period of 30 min a solution of 15.0 g (0.054 mole) of **2b** in 50 ml of tetrahydrofuran. The temperature was kept at 15–25° during the addition; then the mixture was refluxed for 1 hr. The reaction mixture was cooled, and the excess hydride was destroyed by the addition of 10 ml of ethyl acetate. Then 3 ml of water, 2.5 ml of 20% sodium hydroxide solution, and 11 ml of water were added successively to the reaction mixture. The mixture was filtered, and the solid was washed with tetrahydrofuran. All filtrates were combined and evaporated to give 15.0 g of crude **4**, mp 208–214°. Recrystallization from toluene gave 12.6 g of **4**, mp 213–214°. The infrared spectrum of this material was identical with the spectrum of **4** prepared from **1b**.

Registry No.—**1a**, 10037-34-0; **1b**, 10037-35-1; **2a**, 10037-36-2; **2b**, 10037-37-3; **3**, 10037-38-4; **4**, 7538-75-2.

(8) Nmr spectra were recorded on a Varian A-60 spectrometer at 60 Mc. Tetramethylsilane was used as an internal standard.

Selenium Chemistry. II. Stereochemistry of Vicinal Dihalide Elimination

MARTIN PRINCE AND BRUCE W. BREMER

Research Division, School of Engineering, and Science
New York University, University Heights,
New York, New York 10468

Received October 17, 1966

The reaction of 1,2-dihalides with sodium selenide has been reported as a convenient method of preparing alkenes.[1] The synthetic utility of this reaction to the synthesis of stereoisomeric olefin derivatives has been demonstrated by the removal of bromine from 2,3-dibromobutanes by sodium selenide almost entirely in a *trans* elimination at moderate temperatures.

The nature of the elimination of bromine from 2,3-dibromobutanes by sodium selenide was investigated by treating pure *meso*-2,3-dibromobutane and *dl*-2,3-dibromobutane in both dimethylformamide and dimethyl sulfoxide. Gas chromatography was used to analyze the generated butenes.[2]

(1) Paper I: M. Prince, B. W. Bremer, and W. Brenner, *J. Org. Chem.*, **31**, 4292 (1966).

(2) A 50-ft di-*n*-butyl maleate column was used.