the next catalyst addition was delayed until the reaction cooled to 35°. The mixture was stirred for 20 hr at 20–25°; the remaining five 1-g samples of aluminum bromide were added one at a time at 20-min intervals. The mixture was heated at 50° for 13 days.

The mixture was cooled to room temperature. Solvent and excess boron tribromide were removed by vacuum distillation into a series of two Dry Ice–acetone cooled traps. Vacuum was produced by a water aspirator connected to a large safety trap. Solvent removal was speeded by warming the flask with an oil bath set no higher than 40°. The residual reaction mixture was poured on ice, stirred, and then dissolved in methylene chloride. The organic solution was washed with water, 5% sulfuric acid, and water, and then dried with magnesium sulfate.[11] The solvent was removed under vacuum. Hexane was added and the solvent was removed under vacuum to force out remaining bromine and methylene chloride. Although not all of the material dissolved at this point, the mixture was not filtered. The methylene chloride insoluble and hexane insoluble material was mostly C_5Br_6O. The crude yield of II was 851 g.

The crude II was dissolved in 3.5 l. of hot hexane and cooled to room temperature to give a dark solution and additional C_5Br_6O. The solution was split into two equal fractions and each was absorbed on a 3-kg silica gel column (Davison, 200 mesh) and eluted with hexane. The hexane eluent was poured back into the column until the yellow product band began to come off. Six 2-l. fractions were collected from each column. The solvent was removed under vacuum. All of the fractions were combined, since their ir spectra were identical.

Recrystallization from methanol gave 734 g (78%) of high-purity hexabromocyclopentadiene (II), mp 88–90°, with total chlorine 0.05% by X-ray fluorescence.

Hexabromo-3-cyclopentenone (IIIa).—Ketone IIIa, C_5Br_6O (9 g), was separated from the hexane solution of crude II prepared above as nearly colorless crystals, and after elution of II from the silica gel column with hexane, the remaining material was eluted with benzene. The benzene was evaporated under vacuum, and the residue was recrystallized from chloroform to yield 33 g of white crystals. An analytical sample was prepared by three recrystallizations from chloroform: mp 185–188° dec; tlc (carbon tetrachloride with wick) one spot, R_f 0.49; uv $\lambda_{\max}^{\text{cyclohexane}}$ 241 nm (ϵ 14,700), no other max to 400 nm; ir (split mull) C=O at 1841 (w), 1789 (s), 1768 (m), C=C at 1563 cm^{-1} (s).

Anal. Calcd for C_5Br_6O: C, 10.81; Br, 86.31. Found: C, 10.80; Br, 86.70.

Isolation of Other By-products.—Crude II prepared as indicated above was absorbed on silica gel for purification. After elution of II with hexane the remaining material was eluted with hexane–benzene by slowly increasing the percentage of benzene to 50%. Fifteen fractions of 1–2 l. were collected from each column, and the solvent was removed under vacuum. Each fraction was analyzed by tlc. Those fractions having only one or two components were purified further. The only compounds isolated were those which were separated by chance. Many unknown mixtures were discarded.

Fractions 1–9, 2–9, and 2–10 were absorbed on a 350-g silica gel column and eluted with hexane. Nine fractions with a volume increasing from 250 to 2000 ml were collected. Fractions 6–9 were combined. Recrystallization from hexane gave clumps of brown crystals and of off-white crystals. The crystals were separated by hand.

Two recrystallizations of the brown crystals from hexane–methylene chloride gave 0.9 g of V as amber crystals, mp 139–141° dec, tlc (hexane with wick) one spot, R_f 0.35. This material was identical with a sample of $C_{10}Br_{10}$ previously described.[6]

Recrystallization of the off-white crystals from hexane–methylene chloride gave 0.4 g of IV as off-white crystals: mp 135–137° dec; tlc (hexane with wick) one spot, R_f 0.35; ir (CCl_4) CH at 2961 (w), C=C at 1566 (m), max at 1152 cm^{-1} (s); nmr ($CDCl_3$) single line at δ 5.56; mass spectrum, weak P^+ at m/e 614; uv $\lambda_{\max}^{\text{cyclohexane}}$ 244 nm (ϵ 13,000).

Anal. Calcd for C_5HBr_7 (620.5): C, 9.68; H, 0.16; Br, 90.16. Found: C, 10.0; H, <0.3; Br, 90.4.

Column fractions 1–15, 2–14, and 2–16 were combined and recrystallized from hexane–methylene chloride. The first crop (0.5 g) was eluted from a 12 × 2.5 cm silica gel column with benzene to give 0.4 g of brown solid. Two recrystallizations from methylene chloride–carbon tetrachloride gave 0.2 g of VI as yellow crystals, mp 190–192°, identical with a sample of VI prepared by Pews.[9]

Column fractions 1–16, 17, 18, and 2–17, 18, 19 were recrystallized from methanol–methylene chloride to give a mixture of colorless and yellow crystals. Two recrystallizations from methylene chloride–carbon tetrachloride gave 0.3 g of VII as white crystals, mp 172–174° with decomposition and formation of a solid remelting about 215° dec, tlc (benzene with wick) one spot, R_f 0.47. This material was identical with a sample of VII prepared by Pews.[10]

Registry No.—II, 14310-17-9; IIIa (X = Br), 36976-60-0; IVa, 36976-61-1; IVb, 36976-62-2.

Acknowledgment.—The authors are grateful to L. Shadoff for the mass spectral data, to R. Nyquist for the infrared spectra, to J. Heeschen and T. Evans for the nmr data, to L. Swim and P. North for the elemental analyses, and to J. Simek for the uv spectra.

The Synthesis of Cyclic *N*-Cyanoguanidines

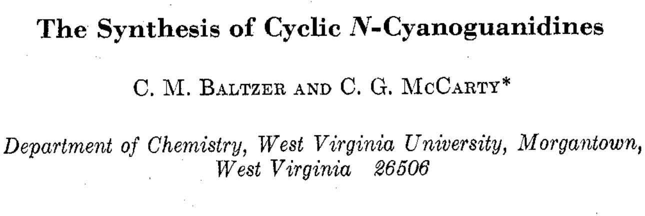
C. M. BALTZER AND C. G. MCCARTY*

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506

Received August 24, 1972

The observation that dimethyl cyanoimidodithiocarbonate (**1**) reacts readily with primary and secondary amines to give *N*-cyanoguanidines[1] prompted us to examine the possible use of **1** with diamines for the synthesis of cyclic *N*-cyanoguanidines. Such cyclic guanidines, not previously reported in the literature, may prove to be as interesting as some of their acyclic analogs which have been studied as hypotensive agents[2] and potential antimalarials.[3]

The reactions of **1** with the various primary and secondary diamines proceed quite readily at the reflux temperature of dry benzene to yield cyclic guanidines with the general formula **2** (Table I).



1

2, R = H, CH_3; x = 2, 3

---

[11] Chlorine-containing impurities in earlier preparations from halogen exchange with methylene chloride during work-up. Slow work-up can drive the product back to very high values of chlorine-containing impurities if the aluminum bromide is not destroyed. A volatile solvent that does not react with aluminum bromide is desired. Benzene gives brominated benzene impurities which are very difficult to remove. Bromine was added as a solvent when early runs at room temperature set up solid. Excess boron tribromide is used on the assumption that $BBrCl_2$ is vented along with BCl_3. When high-purity starting material [purified by vacuum distillation, center cut, bp 108° (10 mm); $n^{25}D$ 1.5625; glc indicated 98% purity] I was used, the crude product could be passed through a single 3-kg column for purification.

(1) C. G. McCarty, J. E. Parkinson, and D. M. Wieland, *J. Org. Chem.*, **35**, 2067 (1970).

(2) S. M. Gadekar, S. Nibi, and E. Cohen, *J. Med. Chem.*, **11**, 811 (1968).

(3) E. L. May, *J. Org. Chem.*, **12**, 437 (1947).

TABLE I

CYCLIC *N*-CYANOGUANIDINES FROM 1[a]

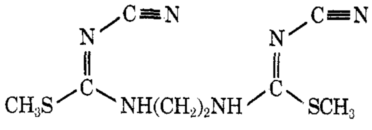
Diamine	Yield, %	Mp, °C	Registry no.
$H_2N(CH_2)_2NH_2$	41	215–216	36982-79-3
$CH_3NH(CH_2)_2NHCH_3$	58	93–94	36982-80-6
$H_2N(CH_2)_3NH_2$	85	186–188	36982-81-7
$CH_3NH(CH_2)_3NHCH_3$	59	34–35	36982-82-8

[a] Satisfactory analytical data (±0.4% for C, H, N) were reported for all compounds listed.

Five- and six-membered rings have been prepared using ethylenediamine, *N*,*N*′-dimethylethylenediamine, 1,3-propanediamine, and *N*,*N*′-dimethyl-1,3-propanediamine in yields of 41–85%.

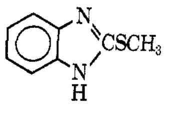
The products all show three distinct bands in the infrared region: 2195–2175 (C≡N), 1630–1550 (C=N), and 1290 cm^{-1} (CN). Their respective nmr spectra are consistent with the assigned structures.

In the case of the reactions using ethylenediamine, the total yield of products was divided between the expected cyclic guanidine (41%) and a compound which proved to be **3** (31%). The reaction gave **3** under a variety of conditions using different solvents, high dilution, inverse addition, etc. Such a side product was not found in any of the reactions with the other diamines. The structure assigned to **3** is consistent with the ir and mass spectral data obtained for it plus the correct microanalysis. Also consistent is the observation that **3** eliminated methyl mercaptan (trapped as the silver mercaptide) when heated to 360°.[1]



$CH_3S-C(=N-C\equiv N)-NH(CH_2)_2NH-C(=N-C\equiv N)-SCH_3$

3



4

The reaction of **1** with *o*-phenylenediamine did not yield the expected cyclic *N*-cyanoguanidine. The product obtained was found to be a benzimidazole (**4**) as reported by D'Amico and coworkers[4] during the course of our investigation.

It is interesting to compare our results with those reported recently by others for the synthesis of cyclic *N*-tosylguanidines from diamines and the *N*-tosyl derivative of **1**. Rodricks and Rapaport[5] apparently observed no product similar to **3** in reactions with ethylenediamine. Also they reported the formation of the expected cyclic guanidine from reactions with *o*-phenylenediamine. On the other hand, their reactions were limited to the synthesis of cyclic guanidines with R = H, since dimethyl *N*-tosylimidodithiocarbonate is unreactive toward secondary amines.

Experimental Section

Melting points were determined with a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Nmr spectra were recorded on a Varian T-60 spectrometer using tetramethylsilane as an internal standard (δ 0.0) and solvents as specified. Ir spectra were recorded on Perkin-Elmer Model 137B and Beckman IR-8 spectrophotometers. Mass spectra were obtained with a Nuclide 12-90-G high resolution, single-focusing spectrometer.

General Procedure.—The reaction involving 1,3-propanediamine will be described. The reactions involving the other diamines were carried out in a similar fashion.

To 20 mmol (1.48 g) of the freshly distilled diamine was added 20 mmol (2.92 g) of dimethyl cyanoimidodithiocarbonate (**1**)[6] in 250 ml of benzene (previously dried over CaH_2). The reaction mixture turned cloudy immediately upon combination of starting materials and the evolution of methyl mercaptan was apparent. The mixture was heated under reflux with stirring for about 6 hr. The white precipitate was filtered from the reaction mixture and air dried. Reduction of the volume of the filtrate yielded no additional material. The crude product was recrystallized from acetone to yield 2.1 g (85%) of white crystals: mp 186–188°; ir (KBr) 3270 (NH), 2150 (C≡N), 1630 (C=N), and 1290 cm^{-1} (CN); nmr (DMSO-d_6) δ 7.5 (s, 2, NH), 3.2 (t, 4, J = 6 Hz, $-CH_2CH_2CH_2-$), 1.8 (quintet, 2, J = 6 Hz, $-CH_2CH_2CH_2-$).

Anal. Calcd for $C_5H_8N_4$: C, 48.4; H, 6.44; N, 45.1. Found: C, 48.1; H, 6.41; N, 44.9.

This reaction (and the others) was successfully repeated several times to establish the reproducibility of the results.

Formation of 3 along with the expected cyclic guanidine from **1** plus ethylenediamine was observed under a variety of conditions, including different solvents (benzene, acetone, absolute ethanol), high dilution, and inverse addition. For example, when 40 mmol (5.48 g) of **1** was added to 40 mmol (2.40 g) of ethylenediamine in 250 ml of dry benzene the mixture immediately turned cloudy. After 4 hr at reflux temperature, the mixture was cooled and the white solid was collected by vacuum filtration. The crude material (4.0 g, mp 203–205°) was separated by fractional crystallization from hot water into 1.62 g of cyclic guanidine (mp 215–216°) and 1.62 g of **3** (mp >350° dec): ir (KBr) 3260 (NH), 2180 (C≡N), 1545 cm^{-1} (C=N); mass spectrum (70 eV) *m/e* 208 ($M^+ - CH_3SH$), 161 ($208 - CH_3S\cdot$).

Anal. Calcd for $C_8H_{12}N_6S_2$: C, 37.5; H, 4.7; N, 32.8; S, 25.0. Found: C, 37.6; H, 4.6; N, 32.9; S, 24.9.

A sample of **3** was heated to 360° in a test tube in a Wood's metal bath while the vapors evolved were led through a trap filled with 5% aqueous $AgNO_3$. The precipitate which formed in the trap ($AgSCH_3$) was collected by filtration. Treatment of this material with a few drops of dilute HCl resulted in the evolution of a gas which was unmistakably methyl mercaptan.

Benzimidazole 4 was formed from the reaction of 20 mmol (2.92 g) of **1** with 20 mmol (2.16 g) of *o*-phenylenediamine in 250 ml of 95% ethanol. After the mixture was heated under reflux for 48 hr the solvent was removed on a rotary evaporator. The brown residue was recrystallized from ethanol–water (3:2) to yield 2.05 g of white crystals: mp 203–205°; ir (KBr) 3060 (CH), 740 cm^{-1} (ortho-disubstituted benzene); nmr (DMSO-d_6) δ 2.7 (s, 3, CH_3), 7.0–7.6 (m, 4, C_6H_4). Further analysis of **4** was not pursued since the report on its identity[5] appeared at this time.

Registry No.—**3,** 36994-48-6; **4,** 7152-24-1.

Acknowledgment.—We gratefully acknowledge support from the National Science Foundation for C. M. B. as an Undergraduate Research Participant during the summer of 1971. Also, we thank Mr. Robert Smith for his help in obtaining the mass spectra.

---

[4] J. J. D'Amico, K. Boustany, A. B. Sullivan, and R. R. Campbell, presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 13–17, 1971.

[5] J. V. Rodricks and H. Rapoport, *J. Org. Chem.*, **36**, 46 (1971).

[6] A. Hantzsch and M. Wolvekamp, *Justus Liebigs Ann. Chem.*, **331**, 265 (1904).

Reaction of *tert*-Butylcyanoketene with Tertiary Amines. Synthesis of 1,3-Di-*tert*-butyl-1,3-dicyanoallene

HAROLD W. MOORE* AND WARREN G. DUNCAN

Department of Chemistry, University of California, Irvine, California 92664

Received July 19, 1972

Reported here is the high-yield conversion of *tert*-butylcyanoketene (**1**) to 1,3-di-*tert*-butyl-1,3-dicyano-