TABLE I

CYCLIC *N*-CYANOGUANIDINES FROM 1[a]

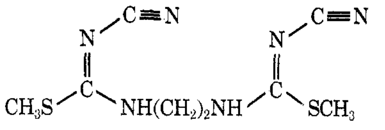
Diamine	Yield, %	Mp, °C	Registry no.
$H_2N(CH_2)_2NH_2$	41	215–216	36982-79-3
$CH_3NH(CH_2)_2NHCH_3$	58	93–94	36982-80-6
$H_2N(CH_2)_3NH_2$	85	186–188	36982-81-7
$CH_3NH(CH_2)_3NHCH_3$	59	34–35	36982-82-8

[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]



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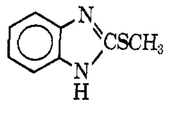

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The reaction of **1** with *o*-phenylenediamine did not yield the expected cyclic *N*-cyanoguanidine. The product obtained was found to be a benzimidazole (**4**) as reported by D'Amico and coworkers[4] during the course of our investigation.

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 $C_5H_6N_4$: 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.

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(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).

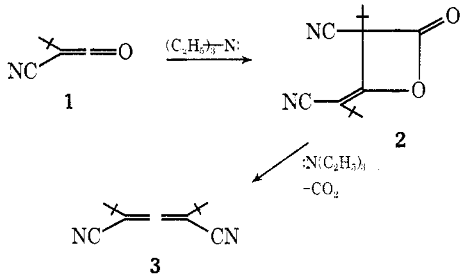
Reaction of *tert*-Butylcyanoketene with Tertiary Amines. Synthesis of 1,3-Di-*tert*-butyl-1,3-dicyanoallene

HAROLD W. MOORE* AND WARREN G. DUNCAN

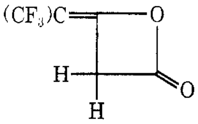
Department of Chemistry, University of California,
Irvine, California 92664

Received July 19, 1972

Reported here is the high-yield conversion of *tert*-butylcyanoketene (**1**) to 1,3-di-*tert*-butyl-1,3-dicyanoallene (**3**) induced by the action of triethylamine at ambient temperature or below. The β-lactone 2 is shown to be an intermediate which subsequently reacts with the amine to give the allene **3**.



The above transformation, accomplished under the reaction conditions reported here, appears to be unique in the chemistry of ketenes. A variety of dimerization pathways for ketenes have been investigated. Farnum and coworkers[1] have proposed that all spontaneous dimerizations of ketenes, except for the parent itself, give 1,3-cyclobutanediones as the major primary products. England and Krespan[2] have investigated the cycloaddition of bis(trifluoromethyl)ketene with a variety of other ketenes to form mixed dimers. Ketene and methylketene were shown to react with bis(trifluoromethyl)ketene giving, respectively, the β-lactones **4** and **5**. Dimethylketene, however, gave a mixture of the β-lactone **6** and the cyclobutanedione **7**. The authors have interpreted these reactions as most likely involving a two-step nonconcerted cycloaddition of the electron-deficient fluoroketene to the carbon–carbon bond of the other cumulene component. *In situ* preparation and dimerization of aliphatic aldoketenes by dehydrohalogenation of the corresponding acid chlorides *via* the action of triethylamine in ether give principally the β-lactone dimers.[1,3-5]



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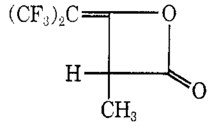

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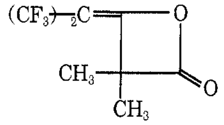

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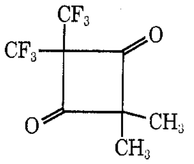

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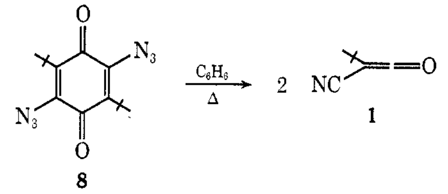
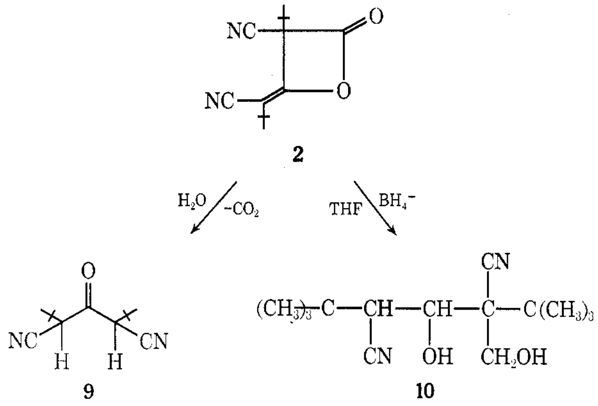
Spontaneous dimerization of *tert*-butylcyanoketene has not been observed. This cumulene is conveniently prepared by the thermal cleavage of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (**8**) in refluxing benzene.[6] The ketene is stable to self-condensation in benzene solution, even at the refluxing temperature for a prolonged period of time (7 days). However, the β-lactone dimer **2** was readily obtained from the ketene **1** by the action of a catalytic amount of triethylamine. It was found that 0.01 equiv of the tertiary amine induced the slow dimerization (8–12 hr) of the ketene in benzene solution giving the β-lactone **2**.



The structure of the β-lactone dimer **2** is in accord with its spectral and chemical properties. Its infrared spectrum (Nujol) showed characteristic carbonyl and alkene absorptions[2,7,8] at 1923, 1865, and 1670 cm^{-1}. The nmr spectrum ($CDCl_3$) showed absorptions for the *tert*-butyl groups at δ 1.32, and the mass spectrum showed a molecular ion at m/e 246 corresponding to 3% of the base peak at m/e 108, which represents the loss of a methyl group from *tert*-butylcyanoketene itself (25% of the base peak). The uv spectrum of **2** in 95% ethanol showed λ_{max} 262 nm. Upon standing in air or upon chromatography over silica gel, hydrolytic decarboxylation takes place, giving the ketone **9**. Analogous transformations have been reported for the β-lactone dimers of diphenylketene[8] and *n*-butylketene.[9] Sodium borohydride reduction of **2** in THF gave a 10% isolated yield of the expected product **10**. Analogous reductions have been reported for tetramethyl-β-propiolactone.[10,11]



A most interesting and, to our knowledge, unprecedented reaction takes place when the β-lactone **2** is treated with 0.1 equiv of triethylamine at ambient temperature. It reacts immediately to give 1,3-di-*tert*-butyl-1,3-dicyanoallene (**3**) in 68% isolated yield. The same allene could be efficiently generated by reacting a benzene solution of *tert*-butylcyanoketene (**1**) with 0.1 equiv of triethylamine (50%) or upon dehydrohalogenation of α-*tert*-butyl-α-cyanoacetyl chloride with the tertiary amine (95%). All of these results are consistent with the following possible mechanism.

The infrared spectrum (Nujol) of the allene **3** shows characteristic absorptions at 2220 (C≡N) and 1945 cm^{-1} (C=C=C). The chemical shift of the *tert*-butyl

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(1) D. G. Farnum, J. R. Johnson, R. E. Hess, T. B. Marshall, and B. Webster, *J. Amer. Chem. Soc.*, **87**, 5191 (1965).

(2) D. C. England and C. G. Krespan, *J. Org. Chem.*, **35**, 3322 (1970).

(3) J. C. Sauer, *J. Amer. Chem. Soc.*, **69**, 2444 (1947).

(4) C. M. Hill and G. W. Senter, *ibid.*, **71**, 364 (1949).

(5) For further discussion of the dimerization of ketenes, see H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, N. Y., 1967; R. N. Lacey in "The Chemistry of the Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964.

(6) H. W. Moore and W. Weyler, *J. Amer. Chem. Soc.*, **92**, 4132 (1970); **93**, 2812 (1971).

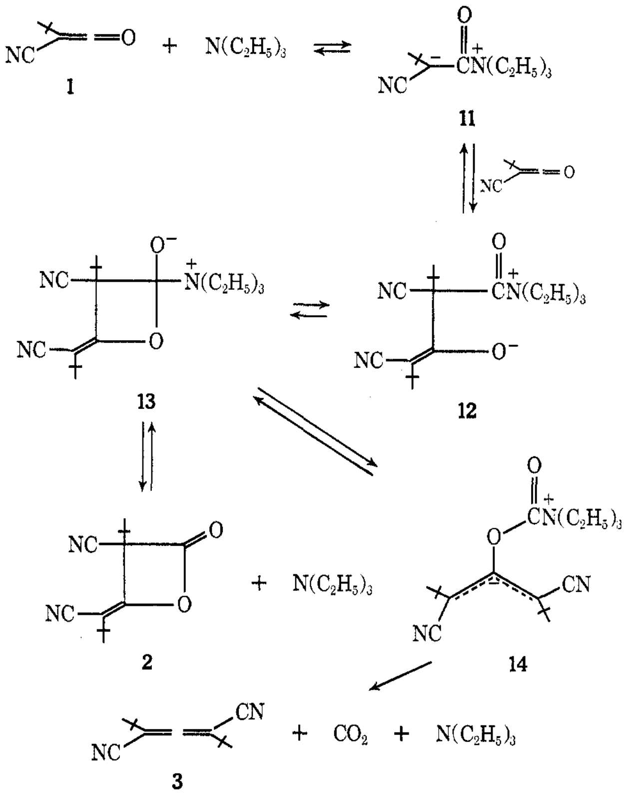
(7) C. J. Pauchert, "The Aldrich Library of Infrared Spectra," Aldrich Chemical Co., Milwaukee, Wis., 1970, pp 206, 310.

(8) R. Anet, *Chem. Ind. (London)*, 1313 (1961).

(9) C. M. Hill and M. E. Hill,[1] *J. Amer. Chem. Soc.*, **75**, 4591 (1953).

(10) G. Natta, G. Mazzanti, G. Pregaglia, and M. Binaghi, *ibid.*, **82**, 5511 (1960).

(11) R. L. Wear, *ibid.*, **73**, 2390 (1951).



groups appear at δ 1.23 (s) in the nmr spectrum (CCl_4), and the mass spectrum shows a molecular ion at *m/e* 202.

Allenes have been generated from *β*-lactone dimers of certain ketenes by high-temperature pyrolysis (150–650°).[12] However, there are no reports in the literature analogous to the facile hydrolytic decarboxylation reported here. Thus, the triethylamine-catalyzed conversion of **2** to **3** appears to be a new reaction. The ease with which this cleavage takes place may be a reflection of the stability of the proposed dicyanoallylcarbanionic intermediate **14**, and thus may be a general reaction for the asymmetrical dimers of cyanoketenes.[13]

Experimental Section

Reaction of *tert*-Butylcyanoketene (1) with 0.01 Equiv of Triethylamine. *β*-Lactone 2.—A solution of 13.3 mmol of *tert*-butylcyanoketene (**1**) was prepared by refluxing 2.0 g (6.67 mmol) of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (**8**) in 20 ml of anhydrous benzene for 2 hr. The benzene solution was cooled to room temperature and 13 mg (0.13 mmol) of triethylamine was added. After 21 hr, an ir spectrum of the reaction solution showed no ketene absorption. The solvent was removed *in vacuo* at 0°, leaving a yellow solid which resisted further purification and recrystallization. It slowly decomposed upon heating and thus showed a broad melting range, 69–79°. However, all of the spectral data for this compound are in agreement with the *β*-lactone structure **2** (*vide supra*).

3,5-Dicyano-2,2,6,6-tetramethyl-4-heptanone (9).—The ketone **9** was prepared in 45% yield by subjecting 0.8 g (3.3 mmol) of the *β*-lactone **2** to chromatography over silica gel. The same ketone could be prepared by allowing a small sample of **2** to stand exposed to the laboratory air for several days. Hexane recrystallization of the 0.35 g of white solid obtained from the silica gel chromatography gave an analytical sample of **9**, mp 108–109°.

Anal. Calcd for $C_{13}H_{20}N_2O$: C, 70.86; H, 9.15; N, 12.71. Found: C, 71.31; H, 8.89; N, 12.67.

Spectral data for **9** follow: ir (Nujol) 2260 (CN) and 1730 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.19 (s, 18, (CH_3—C), 3.57 (s, 2, CH).

3,5-Dicyano-4-hydroxy-3-hydroxymethyl-2,2,6,6-tetramethylheptane (10).—To a solution of 0.5 g (2.2 mmol) of **2** in 25 ml of THF was added 0.18 g (4.8 mmol) of sodium borohydride. This mixture was stirred for 24 hr at room temperature. It was then diluted with water and extracted with dichloromethane. Removal of the solvent gave an oil which partially solidified upon addition of carbon tetrachloride. Filtration gave 50 mg (10% yield) of **10** as a white solid which was recrystallized from chloroform–hexane (1:1) to give the analytical sample, mp 226–227°.

Anal. Calcd for $C_{14}H_{24}N_2O_2$: C, 66.63; H, 9.59; N, 11.10. Found: C, 66.69; H, 9.55; N, 11.10.

Spectral data for compound **10** follow: ir (Nujol) 3350 (OH) and 2265 cm^{-1} (CN); nmr (DMSO-d_6) δ 1.05 (s, 9), 1.15 (s, 9), 3.00 (s, 1), 3.67 (d, 2, J = 4 Hz), 4.18 (d, 1, J = 7 Hz), 5.35 (t, 1, J = 4 Hz), 5.77 (d, 1, J = 7 Hz).

1,3-Di-*tert*-butyl-1,3-dicyanoallene (3). Method A.—To 10 ml of a benzene solution containing 6.7 mmol of the *β*-lactone **2** was added 50 mg (0.5 mmol) of triethylamine. An infrared spectrum taken immediately after addition of the amine showed the disappearance of all bands associated with the *β*-lactone. Thin layer chromatography showed only one spot. Removal of the solvent and purification of the resulting white solid by chromatography gave 0.923 g (68% yield) of the allene **3**, mp 50.5–51.5°.

Anal. Calcd for $C_{13}H_{18}N_2$: C, 77.18; H, 8.97; N, 13.85. Found: C, 77.29; H, 8.90; N, 13.88.

Method B.—To a solution of 10.0 mmol of *tert*-butylcyanoketene (**1**) in 15 ml of benzene was added 30 mg (0.3 mmol) of triethylamine. An infrared spectrum taken immediately showed no ketene absorption. The solvent was removed *in vacuo* and the residue was purified by column chromatography over silica gel. There was collected 0.5 g (50% yield) of the allene **3** which was shown to be identical in all respects with that obtained by method A.

Method C.—A solution of 6.6 mmol of *tert*-butylcyanoketene (**1**) in 10 ml of benzene was cooled in an ice bath and anhydrous hydrogen chloride gas was passed through the solution for 30 min. A solution infrared spectrum showed the absence of ketene absorption and the presence of a carbonyl absorption corresponding to an acyl chloride at 1780 cm^{-1}. Nitrogen gas was then passed through the reaction solution in order to remove the excess hydrogen chloride. The resulting solution was stirred at 0° while adding, dropwise, 0.66 g (6.6 mmol) of triethylamine. The reaction mixture was then extracted with water and the benzene solution was separated and dried over anhydrous sodium sulfate. Removal of the solvent *in vacuo* gave 0.63 g (95% yield) of the allene **3**.

Registry No.—**1**, 29342-22-1; **2**, 36994-51-1; **3**, 36982-41-9; **9**, 36982-42-0; **10**, 36982-43-1.

Acknowledgment.—The authors are grateful to the National Science Foundation for financial support of this work.

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[12] J. C. Martin, U. S. Patent 3,131,234 (1964); *Chem. Abstr.*, **61**, 2969*f* (1964).

[13] The relaxation of possible steric interactions between the two *tert*-butyl substituents in going from the *β*-lactone to the allene may also be of major importance in this reaction.

Relative Rates of Hydroboration of Several Olefins with 4,4,6-Trimethyl-1,3,2-dioxaborinane

RICHARD H. FISH[1]

U. S. Borax Research Corporation,
Anaheim, California

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Recently we have demonstrated the utility of 4,4,6-trimethyl-1,3,2-dioxaborinane (TMDB) as a stable,

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[1] Address correspondence to the Western Regional Research Laboratory, USDA, Berkeley, Calif. 94710.