The Reactions of 1,1,2,2-Tetrachloro-3,4-bis(dichloromethylene)cyclobutane with Amines

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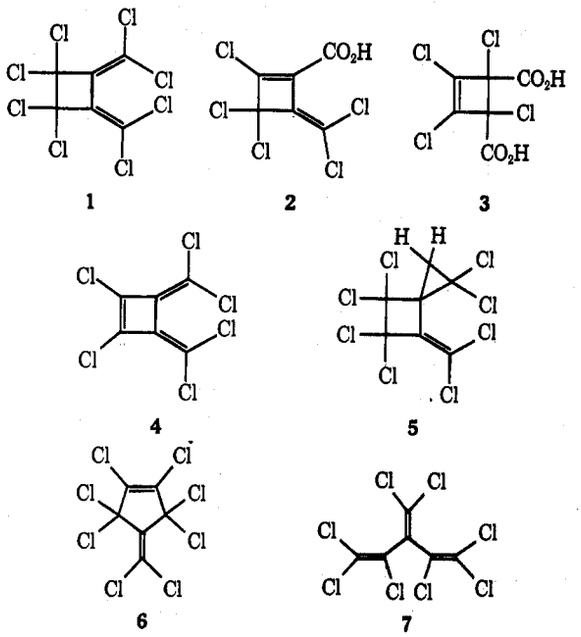
The title compound (1) reacts readily with ammonia to give 2-amino-3,3-dichloro-4-dichloromethylene-1-cyanocyclobutene. With primary or secondary aliphatic or aromatic amines, 1 affords N-substituted 2-alkyl (or aryl) amino-3,3-dichloro-4-dichloromethylenecyclobutenylcarboxamidinium chlorides. The reaction of 1 with phenylhydrazine proceeds with cyclization to give a cyclobutenopyrazole. The spectroscopic properties of these products, and of further transformation products derived from them, are described. A mechanism is proposed for the reaction.

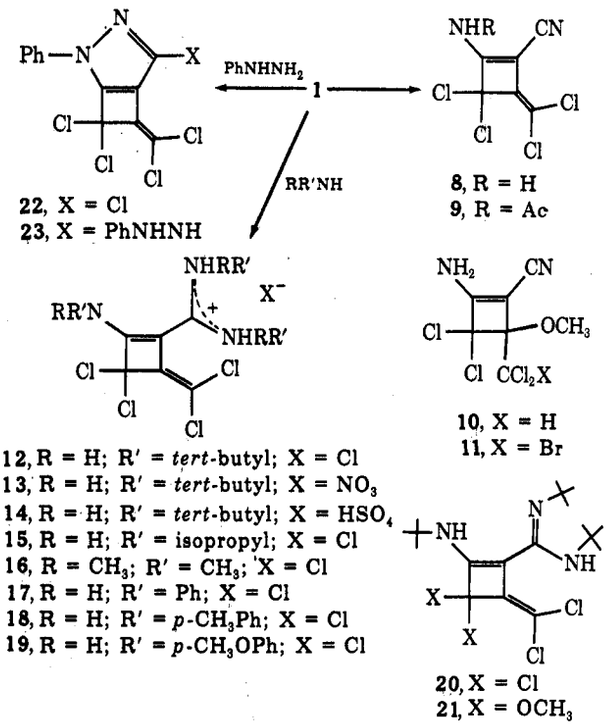
The reactions of small-ring chlorocarbons constitute a relatively unexplored area of organic chemistry. Nitriles,[1] ureas,[2] ketals,[3] oxazolidines,[3] ortho esters,[4] mercaptals,[5] and phenylhydrazones[6] have been prepared by the treatment of chlorocarbons with nucleophiles.

Compound 1,[7] 1,1,2,2-tetrachloro-3,4-bis(dichloromethylene)cyclobutane, which has been reported to yield 2 with sulfuric acid,[8] 3 with fuming nitric acid,[8]



4 with a mixture of aluminum and aluminum chloride,[8] 5 with diazomethane,[9] 6 with aluminum chloride,[10] and 7 upon heating at 230°,[10] was selected as a possible source of novel reactions.

It was felt that the reactive sites of 1 might be susceptible to nucleophilic attack, which would lead to dramatic functional changes. Indeed, reaction of 1 with various amines led to the formation of 8–23.



Results and Discussion

Reaction of 1 with ammonia in aqueous methanol at 4° yielded the aminonitrile 8, whose structure was established by means of spectral data and subsequent reactions. The uv spectrum indicated conjugated unsaturation; the ir spectrum displayed peaks attributable to NH_2 and conjugated nitrile (4.50 μ)[11] and two peaks assigned to C–C double bonds; the mass spectrum showed a molecular ion peak at m/e 242 with an isotopic cluster expected for four chlorine atoms.[12] The existence of an NH_2 was further etablished by the presence of broad, exchangeable protons in the nmr spectrum (which was notably lacking in CH absorp-

(1) (a) H. Khalaf, *Tetrahedron Lett.*, 4223 (1971); (b) S. W. Tobey and R. West, *ibid.*, 1179 (1963),

(2) T. G. Bonner and R. A. Hancock, *Chem. Ind. (London)*, 267 (1965).

(3) R. J. Knopf, *J. Chem. Eng. Data*, **16**, 486 (1971).

(4) H. Khalaf, *Tetrahedron Lett.*, 4239 (1971).

(5) E. P. Ordas, U. S. Patent 2,697,103 to Arvey Corp. (Dec 14, 1954).

(6) A. Roedig, G. Bonse, R. Helm, and R. Kolhaupt, *Chem. Ber.*, **104**, 3378 (1971).

(7) For the synthesis of 1 see W. M. Wagner and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **81**, 925 (1962).

(8) (a) A. Roedig, B. Heinrich, F. Bischoff, and G. Markl, *Justus Liebigs Ann. Chem.*, **670**, 8 (1963); (b) J. Brandmuller and E. Ziegler, *Z. Anal. Chem.*, **200**, 299 (1964).

(9) A. Roedig and B. Heinrich, *Chem. Ber.*, **100**, 3716 (1967).

(10) G. Maahs, *Angew. Chem.*, **75**, 451 (1963).

(11) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Boston, Mass., 1966, p 116. Conjugated nitriles absorb in the 4.48–4.50-μ region, as compared to 4.42–4.46 μ for the unconjugated nitriles.

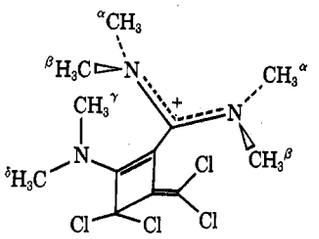
(12) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York, N. Y., 1967, p 22.

tion, thus excluding hydrolytic ring opening) and the formation of the acetyl derivative, **9**. The uv spectrum of **9** differed from that of **8**, suggesting that the amino group was attached to the chromophore.

Reaction of **8** with HCl in aqueous methanol and with bromine in methanol gave the addition products **10** and **11**, respectively. The nmr spectra of both **10** and **11** displayed peaks assigned to methoxy and amine protons. In addition, **10** showed a singlet at τ 3.91, consistent with a hydrogen attached to a carbon bearing two chlorines.[13] The most prominent peak in the mass spectra of both **10** and **11** at m/e 203, corresponded to the loss of CCl_2H and CCl_2Br, respectively, which suggested that **10** and **11** are structurally similar. The uv spectral maxima at 267 and 268 mμ, of **10** and **11**, support this conclusion. It was next decided to investigate the reactions of **1** with amines.

When **1** was treated with *tert*-butyl-, isopropyl-, and dimethylamine, aniline, *p*-toluidine, and *p*-anisidine, a series of compounds with similar properties, was produced and was assigned the amidinium structures **12** and **15–19**. Elemental analysis indicated that each product contained 3 mol of amine. Each amidinium salt possessed a band in its ir spectrum in the 6.15–6.25-μ region which was assigned to the amidinium group.[14] The ionic nature of these salts was established by measuring the electrophoretic mobility of **12** and **16**, conversion of **12** to the nitrate salt **13** and to the bisulfate salt **14**, and reconversion of **14** to **12** by ion exchange. The amidine **20** was prepared from and reconverted to **12**.

The nmr spectra of the amidinium salts were quite revealing. Compound **16** displayed four distinct peaks in D_2O in a 1:2:2:1 ratio. This spectrum can be rationalized in the following manner. The planar amidinium group is prevented by the olefinic chlorine from becoming coplanar with the ring and, therefore,

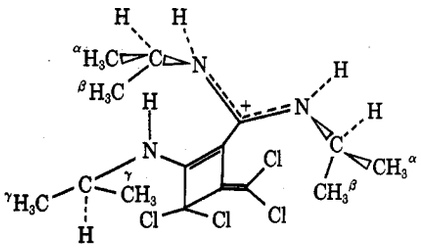


establishes a position orthogonal to the ring. Restricted rotation about the nitrogens of the amidinium group causes the attached methyls to be nonequivalent.[15] Thus the two internal α-methyls and the two external β-methyls form two sets of six identical protons. In addition, restricted rotation about the enamine nitrogen due to electron delocalization can cause the enamine methyls to be nonequivalent.[16] One would therefore expect the nmr spectrum of **16** to show four resonances in a 1:2:2:1 ratio.

The nmr spectrum of **12** in either $CDCl_3$ or C_6D_6–DMSO-d_6 displayed only two singlets, in a 1:2 ratio, for the *tert*-butyl groups. These spectra may be explained by assuming that the *tert*-butyl groups occupy the less crowded external amidinium positions, causing them to be magnetically equivalent. If the enamine *tert*-butyl preferentially occupies one position, or undergoes free rotation about the enamine nitrogen, a 1:2 ratio would be observed.

The isopropylamine product, **15**, displayed three doublets in its nmr spectrum, presumably because the isopropyl groups also occupy the external amidinium positions. Since the plane of symmetry of the molecule does not pass through the isopropyl methine carbons, the methyls of a given isopropyl group are magnetically nonequivalent.[17] However, the α- and β-methyls are equivalent. Since the enamine isopropyl methine carbon can lie in the plane of symmetry, the γ-methyls are equivalent. Each of these methyl absorptions would be split by the methine protons, thus generating the three observed doublets.

In an attempt to produce a cyclobutadiene derivative by a nucleophilic attack at the second dichloromethylene group, **12** was treated with KOH in methanol. However, instead of producing the desired product, the reaction yielded **21**. The equivalence of the methoxyls in it its nmr spectrum established that the product was formed by displacement of the ring chlorines rather than by displacement of the vinyl chlorines.



Because the reaction of **1** with amines had shown the presence of two reactive sites, it was anticipated that a bifunctional amine could produce a heterocyclic product. Phenylhydrazine was selected because attack by both nitrogens would lead to a stable five-membered ring. When **1** was treated with phenylhydrazine in a 1:4 molar ratio (3 mol was used to absorb the HCl which was produced), there was obtained **22**. When the reaction was run with a 1:6 molar ratio, **23** was produced. It was presumably formed by attack of phenylhydrazine on **22**. Strong peaks in the ir spectra of **22** and **23** at 6.58 and 6.64 μ, respectively, were attributed to the pyrazole rings.[18] The location of the phenyl ring in **22** and **23** has been inferred from mechanistic considerations (see the discussion below). However, the alternative structures **24** and **25** cannot be ruled out by the available physical and chemical evidence.

(13) The protons of 1,1,2,2-tetrachloroethane absorb at τ 4.06: F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 252.

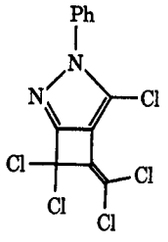
(14) The absorption of the C–N$^+$ bond of amidinium salts has been reported at 5.9–6.3 μ depending upon the specific molecule: (a) J. C. Grivas and A. Taurins, *Can. J. Chem.*, **37**, 1260 (1959); (b) P. Bassignana, C. Cogrossi, G. Polla-Mattiot, and S. Franco, *Ann. Chim. (Paris)*, **53**, 1212 (1963); (c) C. Jutz and H. Amschler, *Chem. Ber.*, **96**, 2100 (1963).

(15) (a) R. C. Neuman, G. S. Hammond, and T. J. Dougherty, *J. Amer. Chem. Soc.*, **84**, 1506 (1962); (b) R. C. Newman and L. B. Young, *J. Phys. Chem.*, **69**, 2570 (1965); (c) G. Scheibe, C. Jutz, W. Seiffert, and D. Grosse, *Angew. Chem., Int. Ed. Engl.*, **3**, 306 (1964).

(16) Several dimethylaminocyclobutenes display separate NCH_3 peaks: R. Breslow, D. Kivelevich, W. Fabian, and K. Wendel, *J. Amer. Chem. Soc.*, **87**, 5132 (1965).

(17) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, Chapter 6.

(18) (a) G. Zerbi and C. Alberti, *Spectrochim. Acta*, **18**, 407 (1962); (b) *ibid.*, **19**, 1261 (1963).



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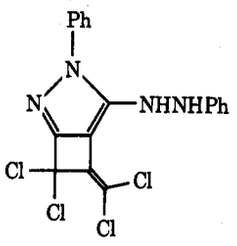

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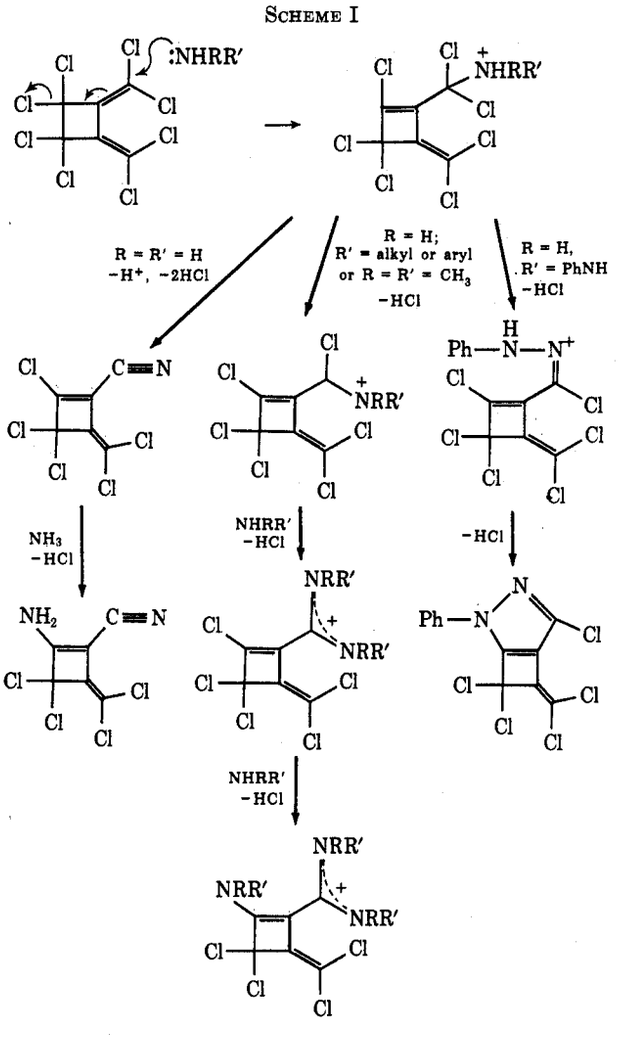
Mechanism of the Reactions.—The following steps are proposed to account for the formation of the products obtained from 1 (Scheme I).

SCHEME I



Initial attack by the amines *via* allylic rearrangement (SN2′), rather than by direct displacement (SN2), is suggested because α halogens accelerate SN2′ reactions[19] and retard SN2 reactions.[20] The formation of 2 from 1 by treatment with KOH presumably occurred *via* the SN2′ mechanism.

Nucleophilic displacement of the second ring chlorine to give either enamines or pyrazoles is reasonable in view of the presence of electron-withdrawing groups in the various intermediates.[21] Further atack by KOH on 2 did not occur, presumably because of the presence of the carboxylate ion.

Displacement of the second vinylic chlorine from the α-chloroimine to give amidinium salts has ample precedent.[22]

Conclusion.—The reactions of 1 with ammonia amines and phenylhydrazine produce nitriles, amidinium salts and pyrazoles, respectively.

Experimental Section

Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. Ultraviolet spectra were determined with a Perkin-Elmer Model 202 spectrophotometer, infrared spectra with a Perkin-Elmer Model 137, and nmr with a Varian A-60 using tetramethylsilane as internal reference. Analyses were performed by Mr. George Robertson, Florham Park, N. J., and Spang Micro-Elemental Laboratory, Ann Arbor, Mich., or by an F & M Elemental Analyzer, Model 185. Mass spectra were determined with a Varian M-66 employing a direct inlet system. Thin layer chromatography was performed on plates prepared with silica gel G or Adsorbosil-1 (Applied Science Laboratories, State College, Pa.) to which approximately 5% Radelin phosphor GS-115 had been added. Column chromatography was performed by using either Fisher reagent grade silica gel, 28–200 mesh, or Mallinckrodt CC7, 28–200 mesh. Ion-exchange chromatography was performed by use of Amberlite IRA-400 (Mallinckrodt Chemical Works).

2-Amino-3,3-dichloro-4-dichloromethylene-1-cyanocyclobutene (8).—Aqueous ammonia (15 ml, 240 mmol), cooled to 4°, was added to a solution of 1 (2.03 g, 5.7 mmol) in 200 ml of absolute ethanol at 4°. After 3 days at 4°, the solvent was removed under vacuum at ambient temperature. The solid residue thus obtained was treated with carbon tetrachloride. The mixture was filtered to remove ammonium chloride. The filtrate was evaporated and chromatographed on silica gel using methanol–chloroform (4:96) as solvent. The major band, R_f 0.38, was collected and yielded 847 mg (61%, colorless crystals, mp 139°) of 8: λ_{max} 262 mμ (ε 8600), 314 (2900); ir (KBr) 2.90, 3.12 (NH_2), 4.50 (C≡N); mass spectrum (70 eV) *m/e* 242 with an isotopic cluster of peaks expected for four chlorines.

Anal. Calcd for $C_6H_2N_2Cl_4$: C, 29.54; H, 0.83; N, 11.49. Found: C, 29.45; H, 0.86; N, 11.11.

2-Acetamido-3,3-dichloro-4-dichloromethylene-1-cyanocyclobutene (9).—Aminonitrile 8 (2.00 g, 8.20 mmol), dissolved in 1 ml of acetic anhydride, was heated at 100° for 48 hr. Upon cooling, a solid slowly precipitated. The mixture was centrifuged. The centrifugate was decanted and treated with an equal volume of water, which caused more solid to deposit. The combined solids were washed with water and crystallized from carbon tetrachloride to afford 1.23 g (52%, colorless crystals, mp 232°) of 9: λ_{max} 265, 341 mμ; ir (KBr) 3.16 (NH), 4.50 μ (C≡N); mass spectrum (70 eV) *m/e* 284, with an isotropic cluster of peaks which indicated four chlorines.

Anal. Calcd for $C_8H_4N_2OCl_4$: C, 33.60; H, 1.41; N, 9.80. Found: C, 33.71; H, 1.37; N, 10.09.

2-Amino-3,3-dichloro-4-dichloromethyl-1-cyano-4-methoxycyclobutene (10).—One milliliter of 5 *N* aqueous hydrochloric acid was added to aminonitrile 8 (100 mg, 0.41 mmol) in 1 ml of methanol. The solution was allowed to stand for 4 days at room temperature. The volume was reduced to approximately 1 ml by a stream of nitrogen. The solid which deposited was collected by filtration and crystallized from chloroform to yield 92 mg (36%, colorless crystals, mp 145–146°) of 10: λ_{max} 267 mμ (ε 11,600); ir (KBr) 2.90, 3.10 (NH); 4.52 μ (C≡N); nmr ($CDCl_3$) τ 3.91 (s, 1 H), 4.20 (broad, 2 H), 6.27 (s, 3 H); mass spectrum (70 eV) *m/e* 274 with an isotopic cluster of peaks which indicated four chlorines.

Anal. Calcd for $C_7H_6N_2OCl_4$: C, 30.46; H, 2.19; N, 10.15. Found: C, 30.90; H, 2.13; N, 10.45.

(19) (a) P. De la Mare and C. Vernon, *J. Chem. Soc.* 3555 (1953); (b) J. D. Park, J. D. Lacher, and J. Dick, *J. Org. Chem.*, **31**, 1116 (1966).

(20) J. Hine, S. J. Ehrenson, and W. H. Brader, *J. Amer. Chem. Soc.*, **78**, 2282 (1956); **77**, 3386 (1955).

(21) S. Patai and Z. Rappaport, "The Chemistry of the Alkenes," Interscience, New York, N. Y., 1964, Chapter 8.

(22) (a) For the synthesis of amidinium salts from α-chloroimines, see H. Paul, A. Weise, and R. Dettmer, *Chem. Ber.*, **98**, 1450 (1965); (b) K. Fujimotom, T. Watanabe, J. Abe, and K. Okawa, *Chem. Ind. (London)*, 175 (1971); (c) for the mechanism, see Z. Rappaport and R. Ta-Shma, *Tetradron Lett.*, 3813 (1971); (d) for a review of the chemistry of α-chloroimines, see H. Ulrich, "The Chemistry of the Imidoyl Halides," Plenum Press, New York, N. Y., 1968.

2-Amino-4-bromodichloromethyl-3,3-dichloro-1-cyano-4-methoxycyclobutene (11).—A solution of one part liquid bromine in two parts methanol was added to aminonitrile **8** (500 mg, 2.05 mmol) in 2 ml of methanol. The mixture was allowed to stand overnight at room temperature and then evaporated to dryness under a stream of nitrogen. The crude solid thus obtained was crystallized from chloroform to yield 220 mg (24%, colorless crystals, mp 151–153°) of **11**: λ_{max} 268 mμ (ε 7500); ir (KBr) 3.05, 3.25 (NH_2), 4.60 μ (C≡N); nmr ($CDCl_3$) τ 3.83 (broad, 2 H), 5.77 (s, 3 H); mass spectrum (70 eV) *m/e* 352, with an isotopic cluster of peaks which indicated one bromine and four chlorine atoms.

Anal. Calcd for $C_7H_5N_2OBrCl_4$: C, 23.69; H, 1.42; N, 7.89. Found: C, 23.73; H, 1.41; N, 7.90.

***N,N'*-Di-*tert*-butyl-2-*tert*-butylamino-3,3-dichloro-4-dichloromethylenecyclobutenylcarboxamidinium Chloride** (12).—*tert*-Butylamine (183 g, 2.50 mol) was introduced dropwise, over a period of 1 hr, into a vigorously stirred solution of **1** (35.6 g, 0.10 mol) dissolved in 350 ml of diethyl ether. The solid (*tert*-butylammonium chloride) which deposited was separated by filtration. The filtrate yielded, upon evaporation, a solid residue which was crystallized from chloroform–hexane to give 30.3 g (65%, colorless crystals, mp 245°) of **12**: λ_{max} 273 mμ (ε 13,600); ir (KBr) 3.38 (NH, CH), 5.86 (exocyclic C=C), 6.20 μ (ring C=C and amidinium); nmr ($CDCl_3$) τ 0.12 (2 H, broad), 2.49 (1 H, broad), 8.55 (9 H, singlet), 8.65 (18 H, singlet); nmr (C_6D_6–DMSO-d_6) τ −0.48 (broad, 2 H), 1.85 (broad, 1 H) 9.03 (s, 9 H), 9.07 (s, 18 H); mass spectrum (70 eV) *m/e* 427.

Anal. Calcd for $C_{15}H_{30}N_3Cl_5$: C, 46.42; H, 6.49; N, 9.02. Found: C, 45.95; H, 6.56; N, 9.12.

Reaction of 12 with Silver Nitrate.—A 5% aqueous silver nitrate solution was added dropwise to a mechanically stirred solution of **12** (150 mg, 0.32 mmol) in 3 ml of methanol, until no further precipitation occurred. The solid was separated by filtration and then treated with chloroform. The mixture was filtered and the filtrate was evaporated to dryness. The solid thus obtained was crystallized from chloroform–hexane to yield the nitrate salt **13** (colorless crystals, mp 230°): λ_{max} 273 mμ (ε 18,500); ir (KBr) 3.08, 3.30 (NH), 3.38 (CH), 5.87 (exocyclic C=C), 6.20 (ring C=C, amidinium), and 7.25 (NO_3^-); nmr identical with that of **12**.

Anal. Calcd for $C_{18}H_{30}N_4O_3Cl_4 \cdot H_2O$: C, 42.37; H, 6.32; N, 10.98. Found: C, 42.42; H, 6.01; N, 10.80.

Reaction of 12 with Sulfuric Acid.—A solution of **12** (300 mg, 0.64 mmol) in 4 ml of 95% ethanol was warmed to 65°. Upon addition of four drops of 18 *M* sulfuric acid, an immediate formation of crystals was observed. The mixture was cooled to room temperature and then filtered. The crystals were recrystallized from chloroform to yield the bisulfate salt **14** (colorless crystals, mp 230° dec): λ_{max} 272 mμ (ε 20,700); ir 3.35 (CH, NH), 5.85 (exocyclic C=C), 6.20 (ring C=C, amidinium), 8.0–8.4 μ (HSO_4^-); nmr (DMSO-d_6) τ 2.17 (broad, 1 H), 7.80 (s, 18 H), 7.90 (s, 9 H); mass spectrum (70 eV) *m/e* 298.

Anal. Calcd for $C_{18}H_{31}N_3Cl_4SO_4$: C, 40.99; H, 5.93; N, 7.97; Cl, 26.40. Found: C, 40.45; H, 5.48; N, 7.78; Cl, 26.61.

Conversion of the Bisulfate Salt 14 to the Chloride Salt 12.—A solution of **14** (145 mg, 0.28 mmol) in 15 ml of 15% water–85% methanol was placed on a column containing 4.5 g of IR-400 anion exchange resin, equivalent to 15 mequiv of exchangeable chloride, in 15% water–85% methanol. The column was washed with 15% water–85% methanol; 30 ml of eluate was collected and then evaporated to dryness. The residue obtained was crystallized from chloroform–hexane to yield colorless crystals of **12**, mp 246–247°. The product was shown to be identical with authentic **12** by comparison of their ir spectra and a mixture melting point.

Reaction of 12 with Potassium Carbonate.—Solid potassium carbonate (470 mg, 3.4 mmol) was added to a vigorously stirred solution of **12** (1.6 g, 3.4 mmol) in a mixture of 240 ml of 95% ethanol and 240 ml of water. At the completion of addition the solution become opaque. Stirring was continued for several hours, during which time a solid deposited. The mixture was evaporated to half volume and filtered. The solid was washed with water, dried in a vacuum desiccator, and crystallized from chloroform–hexane to yield 177 mg (27%, colorless crystals, mp 238°) of *N,N'*-di-*tert*-butyl-2-*tert*-butylamino-3,3-dichloro-4-dichloromethylenecyclobutenylcarboxamidine (**20**): λ_{max} 272 mμ (ε 15,800); ir (KBr) 2.93 (NH), 3.36 (CH, NH), 5.84 (C=C), 6.08 (C=C), and 6.22 μ (amidine); nmr ($CDCl_3$) τ 0.08 (broad, 1 H), 8.42 (s, 9 H), 8.53 (s, 18 H); mass spectrum (70 eV) *m/e* 427.

Anal. Calcd for $C_{18}H_{29}N_3Cl_4 \cdot 2H_2O$: C, 46.46; H, 7.12; N, 9.03. Found: C, 46.44; H, 6.65; N, 9.02.

Conversion of Amidine 20 to Amidinium Salt 12.—A solution of 1 drop of 12 *M* HCl in 1 ml of methanol was added to **20** (43 mg, 0.1 mmol) in 1 ml of methanol. Upon removal of the solvent by a stream of nitrogen, a solid residue was obtained. The ir spectrum of the dry residue (abderhalden pistle, 80°) was identical with that of **12**. A mixture melting point determination of **12** and the product obtained from **20** showed no depression.

Reaction of 12 with Methanolic Potassium Hydroxide.—A 20-ml portion of a freshly prepared and filtered 1.5 *M* solution of potassium hydroxide in methanol was added to **12** (1.6 g, 3.4 mmol) in 24 ml of methanol. The reaction mixture was stirred at room temperature for 5 days, during which time a solid precipitated. The colorless solid was removed by filtration and washed with water to remove potassium chloride, then dried and crystallized from chloroform to yield 503 mg (37%, colorless colorless crystals, mp 222°) of *N,N'*-di-*tert*-butylamino-3,3-dimethoxy-4-dichloromethylenecyclobutenylcarboxamidine (**21**): λ_{max} 278 mμ (ε 14,700); ir (KBr) 3.02 (NH), 3.36 (NH, CH), 5.90 (C=C), 6.30 (amidine), 8.87 μ (ether); nmr ($CDCl_3$) τ −0.20 (broad, 1 H), 6.40 (s, 6 H), 8.53 (s, 18 H), 8.62 (s, 9 H); nmr (DMSO-d_6) τ 0.15 (broad, 1 H), 6.79 (s, 6 H), 8.74 (s, 18 H), 8.81 (s, 9 H); mass spectrum (70 eV) *m/e* 419.

Anal. Calcd for $C_{20}H_{35}N_3O_2Cl_2 \cdot 2H_2O$: C, 52.63; H, 8.61; N, 9.20. Found: C, 52.52; H, 8.00; N, 9.35.

Reaction of Amidine 21 with Dilute Hydrochloric Acid.—To a solution of 150 mg (0.36 mmol) of **21** in 5 ml of tetrahydrofuran was added 4 ml of 0.2 *N* aqueous hydrochloric acid. After several minutes at room temperature, the solution was evaporated to dryness. A solid residue was obtained which was crystallized from chloroform–hexane to yield colorless crystals, mp 232°, of *N,N'*-di-*tert*-butyl-2-*tert*-butylamino-3,3-dimethoxy-4-dichloromethylenecyclobutenylcarboxamidinium chloride (**21**) (HCl): λ_{max} 277 mμ (ε 17,300); ir (KBr) 3.40 (NH, CH), 5.92 (C=C), 6.25 μ (C=C, amidinium).

Anal. Calcd for $C_{20}H_{36}N_3O_2Cl_3$: C, 52.56; H, 7.94; N, 9.20. Found: C, 52.76; H, 8.10; N, 9.07.

Reaction of 1 with Isopropylamine.—A solution of 6.6 g (0.11 mol) of isopropylamine in 50 ml of tetrahydrofuran was added, dropwise, over a period of 3 hrs, to a well-stirred solution of 2.0 g (5.6 mmol) of **1** in 50 ml of tetrahydrofuran. During the addition a solid deposited. The solvent was evaporated to afford an oily mass of crystals, which was treated with chloroform. The undissolved isopropylamine hydrochloride was removed by filtration. Upon evaporation of the chloroform, a solid residue was obtained which was crystallized from chloroform–hexane to yield colorless crystals, mp 218–220° of *N,N'*-diisopropyl-2-isopropylamino-3,3-dichloro-4-dichloromethylenecyclobutenylcarboxamidinium chloride (**15**): λ_{max} 268 mμ (ε 19,100); ir (KBr) 3.40 (CH, NH), 5.82 (C=C), 6.15 μ (C=C, amidinium); nmr ($CDCl_3$) τ 0.49, 0.65 (broad, 3 H), 5.83 (broad) 6.30 (quartet) [The last two peaks integrated together as 3 H. Additional peaks were located at τ 8.55 (d, J = 6.5 cps), 8.64 (d, J = 6.5 cps), and 8.73 (d, J = 6.0 cps). The last three peaks integrated as 18 H.]; mass spectrum (70 eV) *m/e* 447.

Anal. Calcd for $C_{15}H_{24}N_3Cl_5$: C, 42.52; H, 5.71; N, 9.92. Found: C, 42.56; H, 5.60; N, 9.72.

Reaction of 1 with Aniline.—To a solution of 1.00 g (2.80 mmol) of **1** in 20 ml of tetrahydrofuran was added 2.00 g (21.5 mmol) of aniline. After several days at room temperature, the mixture was filtered to remove aniline hydrochloride. Evaporation of the filtrate and treatment with ethyl ether yielded a yellow solid which, upon crystallization from chloroform–carbon tetrachloride, afforded yellow crystals, mp 260°, of *N,N'*-diphenyl-2-anilino-3,3-dichloro-4-dichloromethylenecyclobutenylcarboxamidinium chloride (**17**): λ_{max} 290 mμ (ε 29,100); ir (KBr) 2.95 (NH), 3.50 (CH, NH), 5.87 (C=C), 6.17 (C=C, amidinium), 6.32 μ (aromatic).

Anal. Calcd for $C_{24}H_{18}N_3Cl_5 \cdot H_2O$: C, 53.00; H, 3.71; N, 7.73; Cl, 32.63. Found: C, 52.74; H, 3.39; N, 7.69; Cl, 32.42.

Reaction of **1** with *p*-anisidine and *p*-toluidine was carried out in an analogous manner.

Anal. Calcd for *p*-anisidine product (**19**): C, 52.67; H, 3.93; N, 6.82; Cl, 28.79. Found: C, 52.12; H, 4.12; N, 6.90; Cl, 30.78.

Anal. Calcd for *p*-toluidine product (**18**): C, 57.12; H, 4.26; N, 7.40; Cl, 31.22. Found: C, 56.53; H, 4.08; N, 7.33; Cl, 32.05.

Reaction of 1 with Dimethylamine.—A 250-ml portion of a saturated (10 *M*) solution of dimethylamine in isopropyl alcohol was slowly added to a well-stirred solution of 28.8 g (0.08 mol) of 1 in 250 ml of tetrahydrofuran. The reaction mixture was evaporated to dryness and treated with methylene chloride. The mixture was filtered and the filtrate was evaporated to afford a solid which was crystallized from chloroform–hexane to yield pale yellow crystals, mp 166–167°, of *N,N,N',N'*-tetramethyl-2-dimethylamino-3,3-dichloro-4-dichloromethylenecyclobutenylcarboxamidinium chloride (**16**): λ_{max} 273 mμ (ε 25,300), 372 (6100); ir (KBr) 3.42 (CH), 5.86 (C=C), 6.15 μ (C=C, amidinium); nmr ($CDCl_3$) τ 6.51 (s, 6 H), 6.61 (s, 3 H), 6.71 (s, 6 H), 6.74 (s, 3 H); nmr (D_2O) τ 6.60 (s, 3 H), 6.74 (s, 6 H), 6.84 (s, 6 H), 6.96 (s, 3 H); mass spectrum (70 eV) *m/e* 329.

Anal. Calcd for $C_{12}H_{18}N_3Cl_5 \cdot H_2O$: C, 36.07; H, 5.05; N, 10.52. Found: C, 35.93; H, 4.96; N, 10.58.

Reaction of 1 with Phenylhydrazine.—A solution of 6.05 g (56.0 mmol) of phenylhydrazine in 200 ml of tetrahydrofuran was added dropwise, under a stream of nitrogen, over a period of 2 hr, to a well-stirred solution of 5.0 g (14 mmol) of 1 in 200 ml of tetrahydrofuran. The precipitate which deposited (phenylhydrazine hydrochloride) was removed by filtration. The filtrate was concentrated and chromatographed on Silicar CC-7. Elution was performed with increasing concentrations of chloroform in carbon tetrachloride. Isolated from the column were orange crystals, mp 130°, of 2-phenyl-3,4-(3,3-dichloro-4-dichloromethylene)cyclobuteno-5-chloropyrazole (**22**): λ_{max} 240 mμ (ε 6200), 420 (5200); ir (KBr), 5.92 (C=C), 6.20 (C=C), 6.58 μ (pyrazole); mass spectrum (70 eV) *m/e* 352.

Anal. Calcd for $C_{12}H_5N_2Cl_5$: C, 40.56; H, 1.42; N, 7.90; Cl, 50.01. Found: C, 40.76; H, 1.26; N, 8.04; Cl, 50.02.

Reaction of 1 with Excess Phenylhydrazine.—A solution of 13.0 g (120 mmol) of phenylhydrazine in 200 ml of ethyl ether was added dropwise, under a stream of nitrogen, over a period of 2 hr, to a well-stirred solution of 7.12 g (20 mmol) of 1 in 200 ml of ethyl ether. The precipitate was filtered, washed with water to remove phenylhydrazine hydrochloride, and crystallized from carbon tetrachloride–hexane to yield orange crystals, mp 158° of **23**, ir (KBr) 2.90, 3.00, 6.24, 6.64, 8.02, 8.48, 13.35, and 14.58 μ.

Anal. Calcd for $C_{18}H_{12}N_4Cl_4$: C, 50.73; H, 2.84; N, 13.15; Cl, 33.28. Found: C, 50.57; H, 3.07; N, 13.02; Cl, 32.93.

Registry No.—**1**, 1680-65-5; **8**, 38400-90-7; **9**, 38400-91-8; **10**, 38400-92-9; **11**, 38400-93-0; **12**, 38400-94-1; **13**, 38400-95-2; **14**, 38400-96-3; **15**, 38400-97-4; **16**, 38400-98-5; **17**, 38400-99-6; **20**, 38583-52-7; **21**, 38401-00-2; **21** (HCl), 38401-03-5; **22**, 38401-01-3; **23**, 38401-02-4; ammonia, 7664-41-7; isopropylamine, 75-31-0; aniline, 62-53-3; dimethylamine, 124-40-3; phenylhydrazine, 100-63-0.

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Effect of Geometry and Substituents on the Electrochemical Reduction of Dibenzoylethylenes and Dibenzoylcyclopropanes

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The electrochemical reduction of the geometric isomers of dibenzoylethylene, dibenzoylstyrene, dibenzoylstilbene, dibenzoylcyclopropane, dibenzoylphenylcyclopropane, and dibenzoyldiphenylcyclopropane has been investigated by polarographic and cyclic voltammetric techniques. The polarographic waves were complicated by maxima; hence discussion and conclusions are based on the cyclic voltammetric results. The *cis*- and *trans*-dibenzoylethylenes show a remarkable 267-mV difference in ease of reduction. The dibenzoylethylenes become more difficult to reduce upon successive addition of phenyl groups. The difference between reduction of the geometric isomers of the dibenzoylethylenes reverses from the trans reducing at the more positive potential for dibenzoylethylene to the cis reducing at the more positive potential for dibenzoylstilbene. No discernible trends are observed for the dibenzoylcyclopropanes. The effects of structural changes on reduction potential are discussed.

Chemical reduction of dibenzoylethylenes has been extensively studied by Lutz and coworkers;[2,3] however, the analogous dibenzoylcyclopropanes have received considerably less attention.[4] The reduction of *cis*- and *trans*-dibenzoylethylene by a variety of reducing agents has not shown a demonstrable difference in ease of reduction of these isomers;[3] however, the marked liability of the cis isomer under the reaction conditions suggests that the relative ease of reduction of the cis isomer has not been assessed.[2b,3] On the other hand, preferential and facile reduction of *cis*- over *trans*-dibenzoylstilbene has been observed with $NaBH_4$, $LiAlH_4$, PCl_3, and aluminum isopropoxide.[2b,5] These results have been explained in terms of a "cis-group effect" which presumably arises in part as a result of dipole–dipole interactions of the proximate carbonyl groups and in part from reductions in π-orbital overlap in the cis isomer due to steric crowding. In contradistinction to the above reagents, Zn–HOAc, $SnCl_2$–HOAc–HCl, and sodium hydrosulfite reduce both isomers with apparently comparable ease.[2b,3a] Such differences do not appear to have been reported in the cyclopropane systems. Quantitative assessment of the relative ease of reduction by electrochemical methods should add to the understanding of the reduction of these unsaturated ketones.

There have been only a limited number of investigations comparing the effect of geometry on ease of electrochemical reduction for stereoisomers. *cis*- and *trans*-

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