analogous to the formation of pseudobases from isoquinolinium salts furnishes D. Although proton abstraction from A has been written here as an intramolecular process, it could occur equally well as an intermolecular one. Cyclization by a similar sequence would then give unprotonated D. Only the cis configuration has been shown for C, since it would be the form to cyclize; any trans isomer would through the equilibrium revert to B and ultimately back to *cis*-C.

This reaction scheme is similar to one proposed for the reduction of bisquaternary 1,1′-biisoquinolinium salts by base to air-reactive olefins.[1,3]

Experimental Section

7-Methyl-5,6,10,11-tetrahydro-8*H*-diisoquino[1,2-*c*:2′,1′-*e*]imidazolidiinium Diiodide.—3,3′,4,4′-Tetrahydro-1,1′-biisoquinoline[1] (2, 5.2 g, 0.02 mol) and 8 ml of methyl iodide were refluxed in 100 ml of acetonitrile under a 0° condenser for 18 hr; after the solution had been chilled to 5°, the previously described,[1] dark red dimethiodide was removed, yield 5.7 g (52%).

Addition of ether to the above acetonitrile mother liquors and cooling gave 2.2 g of a mixture of materials. One of these (**3**), comprising about half of the mixture, was less soluble in 80% ethanol than either the monomethiodide or the dimethiodide (both of which were also present) and after several recrystallizations was obtained as pale purple needles with an orange-red hue. The melting point was very indefinite; partial melting, then resolidification at 160–165° with a change in color from purple to pale yellow. (This new solid decomposed at 240–265°.) When plunged into a hot bath at 190–195°, it completely melted; if plunged into a bath at 165°, it partially melted before resolidifying (see following experiment). This compound in methanol did not chemiluminesce in air when made basic: nmr (DMSO-d_6) τ 6.56 (s, 3, -NCH_3), 6.4–7.7 (m, 7), 5.8–6.3 (m, 2, H_6, H_6), 5.22 (d, 1, J = 7.0 Hz, H_8), 4.75 (d, 1, J = 7.0 Hz, H_8), 2.57–2.97 (m, 6, H_2, H_3, H_4, H_{12}, H_{13}, H_{14}), 2.10–2.57 (m, 2, H_1, H_{15}).

Anal. Calcd for $C_{20}H_{22}N_2I_2$: C, 44.15; H, 4.07; N, 5.15; I, 46.64. Found: C, 44.38; H, 3.80; N, 5.10; I, 46.75.

When some of **3** was dissolved in a minimum volume of boiling water and treated with excess sodium bicarbonate, cooling gave a pale yellow solid **5**. Recrystallization from water furnished coarse yellow needles or prisms, mp 177–178° dec; an aqueous solution had an intense blue fluorescence. The ^1H nmr spectrum in DMSO-d_6 was almost identical with that for **3** except that the total proton count was one less. Surprisingly, a mass spectrum showed a small parent peak, m/e 416, with the base peak at m/e 290. The presence of a parent peak suggests opening of the imidazole ring by the nucleophile, iodide ion, to give an iodomethylene derivative.

Anal. Calcd for $C_{20}H_{21}N_2I$: C, 57.70; H, 5.08; N, 6.73; I, 30.49. Found: C, 57.85, 57.80; H, 5.03, 5.08; N, 6.62, 6.73; I, 30.64, 30.35.

The monopicrate from **5** melted at 170–171° after two recrystallizations from absolute ethanol.

Anal. Calcd for $C_{26}H_{23}N_5O_7$: N, 13.53. Found: N, 13.61.

Decomposition of 3.—When **3** was heated for 10 min at 155–165°, there was a 22% loss in weight (theory, 26% for one CH_3I); further heating caused very little more loss. Even when heated at 94° (25 mm) there was an 18% loss of weight in 5 days. The crude product decomposed at 240–260°. Recrystallization from 2-propanol gave yellow blades of 5,6,10,11-tetrahydroiisoquino-[1,2-*c*:2′,1′-*e*]imidazolium iodide (**4**): mp 296–298° dec; nmr (DMSO-d_6) τ 6.83 (t, 4, J = 6.0 Hz, H_5, H_{11}), 5.67 (t, 4, J = 6.0 Hz, H_6, H_{10}), 2.5–2.9 (m, 6, H_2 H_3, H_4, H_{12}, H_{13}, H_{14}), 2.05–2.36 (m, 2, H_1, H_{15}), 0.70 (s, 1, CH in imidazolium ring, H_8).

Anal. Calcd for $C_{19}H_{17}N_2I$: C, 57.01; H, 4.28; N, 7.00; I, 31.71. Found: C, 56.80; H, 4.36; N, 6.93; I, 32.10.

The picrate decomposed at 241–242°.

Anal. Calcd for $C_{25}H_{19}N_5O_7$: N, 13.97. Found: N, 14.00.

Decomposition of 1 in Methanol.—A solution of 0.86 g of **1** in 100 ml of absolute methanol was refluxed for 26.5 hr while protected from moisture. The initially dark red-orange solution became pale orange in color. Cooling for 2 days at 5° deposited 0.36 g of starting compound, mp 208–209° dec; an additional 0.15 g was recovered by evaporating the mother liquors to 20 ml and cooling. Further evaporation to 4–5 ml and cooling gave a mixture of **1** and yellow needles, mp *ca.* 150°, which were separated mechanically. Additional amounts of the latter compound can be isolated by reworking the mother liquors. Recrystallization from 2-propanol gave pale yellow needles, mp 166–167°; the ^1H nmr indicated a mono-2-propanolate. A sample was desolvated at 70° (25 mm) for 24 hr prior to analysis. The nmr spectrum and the analytical data agree with those for **5**.

Anal. Calcd for $C_{20}H_{21}N_2I$: C, 57.70; H, 5.08; N, 6.73; I, 30.49. Found: C, 57.46; H, 5.05; N, 6.67; I, 30.56.

5,6,10,11-Tetrahydro-8-phenyldiisoquino[1,2-*c*:2′,1′-*e*]-imidazolium Perchlorate.—2-Benzyl-3,3′,4,4′-tetrahydro-1,1′-biisoquinolinium bromide[1,4] (0.76 g) in 25 ml of acetonitrile was refluxed for 72 hr. The cooled solution was diluted with a large volume of ether to precipitate a hygroscopic, amorphous solid which was filtered and dried, mp 110–150°; the ^1H nmr spectrum in either $CDCl_3$ or DMSO-d_6 revealed the complete disappearance of the benzyl methylene signal. Since attempts to recrystallize this product were unsatisfactory, it was dissolved in a small volume of water, filtered from insoluble material, and converted to the perchlorate by adding excess sodium perchlorate. This salt, when dry, was easily recrystallized from 2-propanol. The cream-colored crystals turned dark at *ca.* 270° and decomposed at 283–285°: nmr ($CDCl_3$) τ 6.87 (t, 4, J = 6.5 Hz, H_5, H_{11}), 5.83 (t, 4, J = 6.5 Hz, H_6, H_{10}), 2.60 (s, 5, phenyl), 2.16–2.70 (m, 6, H_2, H_3, H_4, H_{12}, H_{13}, H_{14}), 1.94–2.16 (m, 2, H_1, H_{15}).

Anal. Calcd for $C_{25}H_{21}ClN_2O_4$: Cl, 7.89; N, 6.24. Found: Cl, 7.50; N, 6.11.

2-Benzyl-1,1′-biisoquinolinium Bromide.—1,1′-Biisoquinoline (0.6 g) and benzyl bromide (0.4 g) (equimolar ratio) in 10 ml of dry acetonitrile stood at room temperature for 6 days. The former compound gradually dissolved as benzylation occurred. Addition of ether precipitated the monoquaternary salt, which was recrystallized twice from 2-propanol as needles, mp 136–137° dec. The nmr spectrum indicated one propanol of crystallization. The desolvated compound decomposed at 195–197°: nmr (DMSO-d_6) τ 4.18 (s, 2, benzyl CH_2), 2.35–3.22 (complex multiplet, 9, benzyl C_6H_5, H_5', H_6', H_7', H_8'), 2.67 (d, 1, J = 7.0 Hz, H_5), 2.14 (t, 1, J = 7.0 Hz, H_6), 1.73 (t, 1, J = 7.0 Hz, H_7), 1.64 (d, 1, J = 5.5 Hz, H_4'), 1.37 (d, 1, J = 7.0 Hz, H_8), 1.11 (d, 1, J = 5.5 Hz, H_3'), 0.97 (d, 1, J = 7.0 Hz, H_4), 0.62 (d, 1, J = 7.0 Hz, H_3).

Anal. Calcd for $C_{25}H_{19}BrN_2 \cdot C_3H_8O$: C, 68.99; H, 5.58; Br, 16.39; N, 5.75. Found: C, 69.11; H, 5.40; Br, 16.55; N, 5.77.

Refluxing some of the desolvated salt in dry acetonitrile for 72 hr caused no change; the recovered product melted at 194.5–196° and its nmr spectrum was the same as that of the starting material.

Registry No.—**1**, 34414-11-4; **3**, 34410-07-6; **4**, 34414-12-5; **4** monopicrate, 34414-13-6; **5**, 34414-14-7; **5** monopicrate, 34414-15-8; 5,6,10,11-tetrahydro-8-phenyldiisoquino[1,2-*c*:2′,1′-*e*]imidazolium perchlorate, 34414-16-9; 2-benzyl-1,1′-biisoquinolinium bromide, 34414-17-0.

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[3] C. A. Heller and R. A. Henry, unpublished work.

[4] Nmr (DMSO-d_6) τ 6.90 (t, 2, J = 7.5 Hz, H_4'), 6.25–6.72 (m, 2, H_{4eq}, H_{4ax}), 6.10 (t, 1, J = 10.0 Hz, H_{3ax}), 5.82 (doubled triplet, 2, J_t = 7.5 Hz, J_d = 3.0 Hz, H_3'), 5.60 (m, 1, H_{3eq}), 4.55 (s, 2, benzyl CH_2), 2.08–2.70 (m, 5, benzyl C_6H_5).

An Improved Synthesis of *N*-Amino Imides

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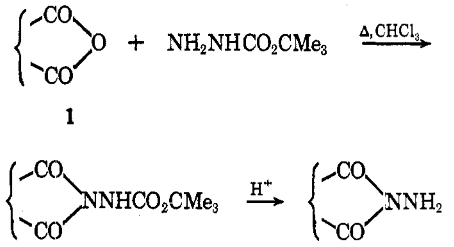
Received June 1, 1971

Depending upon reaction conditions, the reaction of five-membered ring anhydrides with hydrazine can proceed with formation of the cyclic hydrazide, the bishydrazide, the *N*-amino imide, or a mixture of these.[1] Of these products the *N*-amino imide is often the most difficult to obtain. Employing *tert*-butyl carbazate, we have developed a procedure which provides the *N*-amino imide from each of the cyclic anhydrides examined thus far. The series of reactions in generalized form is shown in eq 1.[2] Overall yields are in the range

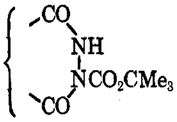


(1)

of 40–80%, and purification of the *N*-*tert*-butyloxycarbonyl amino derivatives **2** is unnecessary for conversion to the *N*-amino imides **3**.

N-Amino imides prepared by this procedure include the *N*-amino derivatives of succinimide **3a**, maleimide **3b**, phthalimide **3c**, *cis*-1,2-cyclohexanedicarboximide **3d**, 3,4-dihydro-1,2-naphthalenedicarboximide **3e**, and 1,2-naphthalenedicarboximide **3f**. The *N*-amino imides **3a–d** had physical properties identical with the literature values. The compounds **3e** and **3f** are new and were characterized by their isomerization to the corresponding cyclic hydrazides which are known[1a] and by their ir spectra. The coupled carbonyl absorptions observed at 1705 and 1760 cm^{-1} for **3e** and at 1720 and 1770 cm^{-1} for **3f** are characteristic of *N*-amino maleimides.[1a]

Proof of the structures for **2a–f** as formulated in eq 1 rather then structures of the type **4** includes the fact that all carbonyl absorptions are above 1700 cm^{-1}. This indicates five-membered rather than six-membered lactam rings, for which carbonyl positions are characteristically in the range 1650–1670 cm^{-1}.[1a] Isomaleimide structures of the type **5** are also untenable in view of the uv spectra of **2b**, **2c**, **2e**, **2f**, **3e**, and **3f**. Maleimides are known to absorb in the uv at about 220 (log ϵ 4–4.25) and 300 nm (log ϵ 2.7), while isomaleimides absorb at 300 nm (log ϵ 4.3).[3] All of the compounds in question have intense uv absorption between 217 and 229 nm (log ϵ 4–4.5) and weak absorption at 300 nm (log ϵ 3.4) and, in this respect, resemble the maleimides. The structure of **2c** is certainly not of the isomaleimide type, since this specific compound **6** has been reported,[2] and the reported melting point of **6** is 55° lower than our observed melting point for **2c**.



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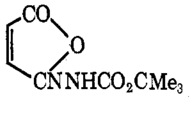

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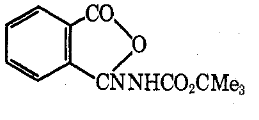

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We feel that the method outlined in eq 1 will prove to be generally applicable for the conversion of five-membered ring anhydrides to *N*-amino imides, thereby obviating the difficulties normally encountered in their preparation from the anhydride and hydrazine.

Experimental Section

Infrared spectra were recorded in Nujol; ultraviolet spectra were recorded in 95% ethanol.

***N*-Aminosuccinimide (3a).**—Succinic anhydride (0.01 mol) and *tert*-butyl carbazate (0.01 mol) were dissolved in 15 ml of chloroform. The solution was refluxed for 3 hr, and the solvent was evaporated *in vacuo* to leave an oil, ir 1720 cm^{-1}, which was dissolved in 5 ml of methanol without purification. The solution was cooled to 5°, and a slow stream of anhydrous hydrogen chloride was passed into the solution for 10 min. The resulting mixture was left to stand at 20° for 2 hr and diluted with 20 ml of ether. The solid was filtered at the pump and treated with 10 ml of an anhydrous solution of ammonia in methanol. The precipitated NH_4Cl was removed by filtration, and the filtrate was evaporated to dryness to yield 0.9 g (80%) of **3a**, which was identified as the diacetate, mp 73–74° (lit.[4] mp 70–72°).

***N*-Aminomaleimide (3b).**—This compound was prepared as described above from maleic anhydride and was isolated in 75% yield as the hydrochloride salt, mp 145–148° (lit.[5] mp 150°). As before, the residue resulting upon evaporation of the chloroform was an oil which was not purified before treatment with HCl–methanol. This oil had ir 1700 cm^{-1}, uv 220 nm (log ϵ 4.15).

***N*-*tert*-Butyloxycarbonylaminophthalimide (2c).**—This compound was prepared from phthalic anhydride as described above in 85% yield: mp 185–186° (ethanol); ir 1710 and 1780 cm^{-1}; uv 220 nm (log ϵ 4.49) and 295 (3.45).

Anal. Calcd for $C_{13}H_{14}N_2O_4$: C, 59.53; H, 5.38; N, 10.69. Found: C, 59.45; H, 5.31; N, 10.80.

***N*-Aminophthalimide (3c).**—The entire product **2c** from above was treated with HCl–methanol to obtain the hydrochloride salt of **3c**, which was converted to the free imide upon treatment with aqueous $NaHCO_3$ in 95% yield: mp 200–205°, solidifies and remelts at 338–340° (lit.[6] mp 200–205°, solidifies and remelts at 340°); ir 1715 and 1775 cm^{-1}; uv 222 nm (log ϵ 4.49) and 298 (3.38).

***cis*-*N*-Amino-1,2-cyclohexanedicarboximide (3d).**—The compound **2d**, which resulted upon reaction of *tert*-butyl carbazate and *cis*-1,2-cyclohexanedicarboxylic acid anhydride, was obtained as a gummy material which was not characterized except for its ir spectrum, 1715 and 1785 cm^{-1}. Successive treatment of **2d** with HCl–methanol and NH_3–methanol as described above gave **3d** in 85% yield, mp 60–63° (lit.[1c,7] mp 63–64°).

***N*-*tert*-Butyloxycarbonylamino-3,4-dihydro-1,2-naphthalenedicarboximide (2e).**—This compound was prepared from the corresponding anhydride as described above in 90% yield: mp 172–173° (benzene–hexane); ir 1730 and 1780 cm^{-1}; uv 229 nm (log ϵ 4.19) and 365 (3.60).

Anal. Calcd for $C_{17}H_{18}N_2O_4$: C, 64.95; H, 5.77; N, 8.91. Found: C, 65.17; H, 6.09; N, 8.84.

***N*-Amino-3,4-dihydro-1,2-naphthalenedicarboximide (3e).**—The product **2e** was treated with 10 ml of hydrofluoric acid at 40° until gas evolution ceased. The solution was poured into ice-water, and the solid was filtered at the pump, washed with aqueous $NaHCO_3$ solution, and air dried to give **3e** (70%): mp 156–158°; ir 1705 and 1760 cm^{-1}; uv 234 nm (log ϵ 4.0) and 374 (3.43).

Anal. Calcd for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.70; N, 13.08. Found: C, 67.01; H, 4.82; N, 12.90.

Compound **3e** was further characterized by its isomerization in refluxing *n*-butyl alcohol to the corresponding cyclic hydrazide, mp 230–234° (lit.[1a] mp 231–232°).

***N*-*tert*-Butyloxycarbonylamino-1,2-naphthalenedicarboximide (2f).**—This compound was prepared from the corresponding anhydride in 90% yield: mp 207–209° (benzene–hexane); ir

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[1] (a) F. G. Baddar, M. F. El-Newaihy, and M. R. Salem, *J. Chem. Soc. C*, 716 (1971); (b) H. Feuer, G. B. Bachman, and E. H. White, *J. Amer. Chem. Soc.*, **73**, 4716 (1951); (c) E. Grovenstein, D. V. Rao, and J. W. Taylor, *ibid.*, **83**, 1705 (1961).

[2] A similar but less convenient procedure utilizing benzyl carbazate in place of *tert*-butyl carbazate has been reported by L. A. Carpino, *J. Amer. Chem. Soc.*, **79**, 98 (1957).

[3] E. Hedaya, R. L. Hinman, and S. Theodoropulos, *J. Org. Chem.*, **31**, 1311 (1966).

[4] Th. Curtius, *J. Prakt. Chem.*, **92**, 80 (1915).

[5] H. Hinterbauer, Austrian Patent 176,563 (Nov 10, 1953).

[6] H. D. K. Drew and H. H. Hatt, *J. Chem. Soc.*, 16 (1937).

[7] M. Ishikawa, M. Fujimoto M. Sakai, and A. Matsumoto, *Chem. Pharm. Bull.*, **16** (4), 618 (1968).

1735 and 1785 cm^{-1}; uv 217 nm (log ϵ 4.47), 258 (4.47), and 345 (3.43).

Anal. Calcd for $C_{17}H_{16}N_2O_4$: C, 65.37; H, 5.16; N, 8.97. Found: C, 65.28; H, 5.23; N, 9.05.

***N*-Amino-1,2-naphthalenedicarboximide (3f).**—This compound was prepared from **2f** by the same method used for preparation of **3e**. The yield was 80% for **3f**: mp 196–197°; ir 1720 and 1770 cm^{-1}; uv 218 nm (log ϵ 4.59), 258 (4.51), and 346 (3.32).

Anal. Calcd for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; N, 13.20. Found: C, 67.98; H, 3.81; N, 13.32.

Compound **3f** was further characterized by its isomerization in refluxing *n*-butyl alcohol to the corresponding cyclic hydrazide, mp 332–335° (lit.[1a] mp 340°).

Registry No.—**2c**, 34387-89-8; **2e**, 34387-90-1; **2f**, 34387-91-2; **3e**, 34387-92-3; **3f**, 34387-93-4.

Acknowledgment.—We thank the Niagara University Research Council for its generous support.

Hydrogen Abstraction from Arylmethanes by Bromine Atom

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Received November 23, 1971

An excellent correlation of the relative rates of hydrogen abstraction from a series of arylmethanes by the trichloromethyl radical with the change in SCF-π-binding energies between the incipient radicals and the arylmethanes recently has been reported.[2] No such correlation was found for abstraction by *tert*-butoxy radical.[2] Unruh and Gleicher[2] interpret this as evidence that the transition state for hydrogen abstraction by the trichloromethyl radical must strongly resemble the intermediate free radical while that for abstraction by *tert*-butoxy radical probably has a structure between the reactant and the intermediate. We wish to report a similar study in which bromine atom is the abstracting species.

Competitive brominations were carried out at 75.5° using standard techniques.[3] Analysis of the resulting arylmethyl bromides was done by nmr techniques so that ring substitution in arenes by bromine atom was not an analytical problem. The results are reported in Table I. Unfortunately, 2-methylanthracene, 9-methylanthracene, and 1-methylpyrene did not afford benzylic bromination but rather a rapid ring substitution reaction. As a result, the kinetic results have a spread of only about six.

Table I

Relative Rates of Hydrogen Abstraction by Bromine in Benzene at 75°

Arylmethane	No. of expt	k/k_0[a]
Toluene		(1.00)
2-Methylphenanthrene	3	2.03 ± 0.03
2-Methylnaphthalene	3	2.72 ± 0.01
3-Methylphenanthrene	6	3.19 ± 0.32
1-Methylphenanthrene	3	4.00 ± 0.13
1-Methylnaphthalene	3	5.69 ± 0.05

[a] Experimental error represents average deviation of the number of experiments shown.

Table II

Correlations of the Relative Rates of Hydrogen Abstraction from Unsubstituted Arylmethanes by Bromine Atom with Various Molecular Orbital Parameters

Parameter	Correlation coefficient
HMO charge density	0.947
SCF ΔE_π[a]	0.935
SCF charge density	0.934
HMO free valence	0.899
HMO ΔE_π	0.898

[a] Values taken from ref 2.

Correlation of the natural logarithms of the relative rates of hydrogen abstraction with some calculated molecular orbital parameters are shown in Table II. While none of the correlations are as excellent as that obtained by Unruh and Gleicher[2] for trichloromethyl radical with SCF ΔE_π, it is interesting to note that all are good. Charge density calculations[4] were made using an arylmethyl cation as a model and the correlation was made with charge density at the methyl carbon atom. It is not clear what such a correlation represents, especially from the somewhat surprising result that the Hückel method gives better results than does the SCF approach. One is tempted to explain the correlation with charge density on the basis of the suggestion of Russell and Williamson[5] of stabilization of the transition state by a significant contribution of a polar canonical structure I. On the basis of the rather good correlation with the SCF ΔE_π parameter and the interpretation given to such a correlation by Unruh and Gleicher,[2] the transition state for the hydrogen abstraction by bromine atom must strongly resemble the radical intermediate.

$$\mathrm{ArCH_2H\cdot X} \longleftrightarrow \underset{\mathbf{I}}{\mathrm{Ar\overset{+}{C}H_2H\overset{-}{X}}} \longleftrightarrow \mathrm{ArCH_2H\text{-}X}$$

Experimental Section

All methylarenes were commercially available. Toluene and benzene were distilled as constant-boiling heart cuts.

Brominations were run at 75.5° in a 50-ml, three-necked flask fitted with a nitrogen bubbling tube, a water condenser, and an addition funnel. Hydrocarbons to be studied were weighed into the flask and benzene was added so that the total initial concentration was about 0.2 *M*. After the flask was placed in the constant-temperature bath the solution was degassed with bubbling nitrogen. A benzene solution of bromine was added slowly with irradiation of the solution with 275-W Sylvania sunlamp. The rate of addition was adjusted so that the reacting solution remained nearly colorless. Evolved hydrogen bromide was entrained by bubbling nitrogen through the solution, which also served to agitate the solution. Upon completion of the reaction, about 15 min, the mixtures were reduced to a volume of approximately 2 ml on a rotary evaporator at room temperature and 80–140 mm pressure. Ethylene dichloride was weighed into the concentrated solution as a standard and the arylmethyl

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[1] (a) National Science Foundation, COSIP participant; (b) National Science Foundation, URP participant.

[2] J. D. Unruh and G. J. Gleicher, *J. Amer. Chem. Soc.*, **93**, 2008 (1971).

[3] R. D. Gilliom and B. F. Ward, Jr., *ibid.*, **87**, 3944 (1965).

[4] HMO calculations were made utilizing the program of J. R. Howles and R. D. Gilliom, "Huckel," Program 132, Quantum Chemistry Program Exchange, Indiana University. SCF charge density calculations were made using J. E. Bloor and B. R. Gilson, "SCFCIO-Closed-Shell SCF-LCAO-MO," Program 71.2, Quantum Chemistry Program Exchange, Indiana University, rewritten in SPS for calculations on an IBM 1620-40K.

[5] G. A. Russell and R. C. Williamson, Jr., *J. Amer. Chem. Soc.* **86**, 2357 (1964).