cyclohexanone: ir 3.41, 5.86, 6.82, 6.96, 7.28, 7.36, 7.40, 7.50, and 8.50 μ; nmr ($CDCl_3$) τ 7.68 (m, 4, CH_2CO, 7.80–9.00 (m, 13, CH), 9.07 (s, 3, CH_3), 9.13 (s, 3, CH_3), and 9.05–9.22 (3, $CHCH_3$).

This material crystallized upon standing and was recrystallized from hexane; mp 48.5–49.5°.

Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.60; H, 11.34.

4-(*exo*-5-*exo*-Isocamphyl)cyclohexene (5).—A mixture of 59 g (0.25 mol) of *cis*- and *trans*-4-(*exo*-5-*exo*-isocamphyl)cyclohexanol (**2** and **3**), 300 ml of *p*-menthane, and 0.5 g of 85% phosphoric acid was refluxed with a Dean–Stark water separator until no more water was produced. An additional 0.5 g of 85% phosphoric acid was added, and refluxing was continued until no more water was produced and the theoretical amount had been collected (12 hr). The mixture was washed with water, 10% sodium carbonate, and again with water. The solvent was removed at 20 mm. The product was distilled through a 37-cm column packed with glass helices. The yield was 49 g (0.224 mol, 90%) of 4-(*exo*-5-*exo*-isocamphyl)cyclohexene (**5**), homogeneous by vapor phase chromatography: bp 83° (0.2 mm); $n^{20}D$ 1.5003; ir 3.38, 3.50, 6.10, 6.87, 6.98, 7.05, 7.30, 7.39, 7.42, 7.52, 7.70, 8.05, 8.48, 8.80, 9.10, 9.71, 10.10, and 13.70 μ; nmr ($CDCl_3$) τ 5.40 (d, 2, J = 3.5 cps, *cis* HC=CH), 7.95–9.05 (br, 15, CH), 9.10 (s, 3, CCH_3), 9.17 (s, 3, CCH_3), and 9.05–9.35 (3, $CHCH_3$).

Anal. Calcd for $C_{16}H_{26}$: C, 88.00; H, 12.00. Found: C, 87.97; H, 11.96.

***cis*- and *trans*-1,2-Epoxy-4-(*exo*-5-*exo*-isocamphyl)cyclohexane (6 and 7).**—To a solution of 9.00 g (41.2 mmol) of 4-(*exo*-5-*exo* isocamphyl)cyclohexene (**5**) in 90 ml of methylene chloride was added at room temperature in small quantities 8.8 g (43.2 mmol, 85% pure) of *m*-chloroperbenzoic acid with constant stirring. After the addition was complete, the mixture was stirred for 60 hr at room temperature. The resulting mixture was filtered and the solvent was removed under reduced pressure. The residue was taken up in ether, washed with 3% sodium hydroxide and water, and dried ($MgSO_4$). The ether was removed, producing 8.21 g of product which was 88.5% pure by vapor phase chromatography (0.035 mol, 85%). This mixture had a woody, sandalwood odor. A Versamide column (225°) showed two components (*cis* and *trans* isomers) in a 1:1 ratio, but preparative separation was not possible. The product was distilled through an 8-in. Vigreux column: bp 123° (1.3 mm); $n^{20}D$ 1.5032; ir 3.40, 6.80, 6.90, 7.00, 7.22, 7.30, 7.33, 7.45, 7.90, 8.50, 10.30, 11.70, 12.30, 12.60, and 13.50 μ; nmr τ 6.92–7.17 (br, 2, HCOCH), 7.90–9.00 (br, 15, CH), 9.17 (s, 3, CCH_3), 9.21 (s, 3, CCH_3), and 9.03–9.23 (3, $HCCH_3$).

Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.54; H, 10.77.

***trans*-3-(*exo*-5-*exo*-Isocamphyl)cyclohexanol (10) and *cis*-4-(*exo*-5-*exo*-Isocamphyl)cyclohexanol (8).**—To a solution of 70.0 g of lithium aluminum hydride in 2100 ml of dry ether was added, dropwise with cooling, 322 ml of a solution of 93.25 g of anhydrous aluminum chloride in 700 ml of dry ether.[7] A mixture of 54.5 g (0.25 mol) of *cis*- and *trans*-1,2-epoxy-4-(*exo*-5-*exo*-isocamphyl)cyclohexane (*ca.* 1:1) dissolved in 1000 ml of dry ether was added dropwise with stirring and cooling to room temperature to the above solution. After the addition was complete, the mixture was allowed to stand at room temperature for 0.5 hr. The excess hydride was decomposed by the dropwise addition of isopropyl alcohol followed by wet ether. The organic phase was separated, the water layer was extracted several times with ether and dried ($MgSO_4$), and the solvent was removed under atmospheric conditions. There was produced 54.1 g (0.23 mol, 92%) of a mixture of *trans*-3-(*exo*-5-*exo*-isocamphyl)cyclohexanol (**10**) and *cis*-4-(*exo*-5-*exo*-isocamphyl)cyclohexanol (**8**). The two axial alcohols **8** and **10** could not be separated by vapor phase chromatography, but the trimethylsilyl ethers and trifluoroacetic esters could be separated. The mixture of **8** and **10** had ir 3.15, 3.50, 6.95, 7.36, 8.00, 8.45, 8.80, 9.50, 10.35, 11.35, 12.35, and 12.95 μ; nmr ($CDCl_3$) τ 5.78–6.10 (br, 1, CHO), 8.10–9.05 (br, 18, CH and OH), 9.12 (s, 3, CCH_3), 9.19 (s, 3, CCH_3), and 9.05–9.20 (3, $CHCH_3$).

Anal. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94. Found: C, 80.65; H, 12.00.

Separation of *trans*-3-(*exo*-5-*exo*-Isocamphyl)cyclohexanol (10) and *cis*-4-(*exo*-5-*exo*-Isocamphyl)cyclohexanol (8) *via* Trimethylsilyl Ether Derivatives.—To a solution of 20 g (85 mmol) of *trans*-3-(*exo*-5-*exo*-isocamphyl)cyclohexanol (**10**) and *cis*-4-(*exo*-5-*exo*-isocamphyl)cyclohexanol (**8**) in 1 l. of dry pyridine was added 200 ml of hexamethyldisilazane followed by 80 ml of trimethylchlorosilane at room temperature. After the addition was complete the mixture was stirred at room temperature for 1 hr. The solvent and unreacted starting materials were removed under water pump vacuum. The last traces of solvent were removed by heating to 100° at 1 mm. The crude product weighed 22.7 g (74 mmol, 87%). The product was distilled as follows through a Teflon spinning band column. The crude material weighed 22.4 g and was composed of 41.8% **9** and 58.2% **11**. The fraction with bp 98–100° (0.028–0.035 mm) contained 4.8 g of the trimethylsilyl ether of *trans*-3-(*exo*-5-*exo*-isocamphyl)-cyclohexanol. The fraction with bp 100–202° (0.029–0.038 mm) contained 2.2 g of the trimethylsilyl ether of *cis*-4-(*exo*-5-*exo*-isocamphyl)cyclohexanol. Each of the above pure isomers was refluxed for 8 hr with 5% water in methanol (500 ml). The pure alcohols were obtained by evaporation of the methanol and removal of the water in theoretical yield.

The pure ***trans*-3-(*exo*-5-*exo*-isocamphyl)cyclohexanol (10)** was obtained as a colorless, viscous oil which, after several weeks storage, started to crystallize. Even after many months, it failed to solidify completely. Attempts at recrystallization from a variety of solvents were unsuccessful. Except for this behavior on crystallization, **10** appeared to be homogeneous (ir, nmr, vpc on several columns). We believe that our product is a mixture of isomers **10** and **12**. It analyzed as follows: $n^{20}D$ 1.5001; ir 2.99, 3.42, 6.90, 7.20, 7.25, 7.30, 7.90, 8.80, 9.05, 9.50, 10.05, and 10.30 μ; nmr ($CDCl_3$) τ 5.94 (centered, br, 1, CHO), 8.20–9.03 (br, 18, CH and OH), 9.11 (s, 3, CH_3), 9.28 (s, 3, CCH_3), and 9.00–9.20 (3, $CHCH_3$); mass spectrum m/e 236 (M^+).

Anal. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94. Found: C, 81.03; H, 12.02.

This alcohol has a strong sandalwood odor. The proton on the carbon atom bearing the hydroxyl group appears at τ 5.94, which is consistent with an equatorial proton and therefore an axial alcohol. The 10.3-μ band in the ir, characteristic of axial alcohols, confirms the structure.[5]

The pure ***cis*-4-(*exo*-5-*exo*-isocamphyl)cyclohexanol (8)** was obtained as a colorless crystalline material which could be recrystallized from hexane: mp 88–89°; ir 2.98, 3.45, 6.88, 7.22, 7.30, 7.34, 7.92, 8.77, 9.42, 9.70, 9.87, 10.30, 10.50, 11.10, 11.25, 11.55, 12.30, and 12.50 μ; nmr τ 6.05 (centered, br, 1, CHO), 8.20–9.00 (br, 18, CH and OH), 9.08 (s, 3, CCH_3), 9.16 (s, 3, CCH_3), and 9.00–9.20 (3, $HCCH_3$); mass spectrum m/e 236 (M^+).

Anal. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94. Found: C, 80.93; H, 12.01.

This alcohol was odorless. The proton on the carbon atom bearing the hydroxyl group appears at τ 6.05, which is consistent with an equatorial proton and therefore an axial alcohol. The 10.3-μ band in the ir, characteristic of axial alcohols, confirms the structure.[5]

Registry No.—**2**, 22242-60-0; **3**, 22242-61-1; **4**, 22242-62-2; **5**, 22242-67-7; **6**, 22242-63-3; **7**, 22242-64-4; **9**, 22297-77-4; **10**, 22242-65-5; **11**, 22242-66-6.

Conformations of Cyclic Peptides. Stability of Folded Conformations of *para*-Substituted 3-Benzylpiperazine-2,5-diones[1]

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Cyclic dipeptides bearing an arylmethyl side chain, *e.g.*, 3-benzylpiperazine-2,5-dione (cycloglycylphenyl-

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TABLE I

TEMPERATURE DEPENDENCE OF 2,5-PIPERAZINEDIONE CH PROTON CHEMICAL SHIFTS, $\delta = A - B$

Piperazinedione	Solvent	A (σ_A), ppm[a,b]	10^4B (σ_B),[b] ppm/deg
Unsubstituted	CD_3COOD	4.140 (0.004)	7.1 (0.5)
Unsubstituted	$CF_3COCF_3\cdot 1^1/_2D_2O$	4.125 (0.005)	4.0 (0.5)
Unsubstituted	CF_3COOH	4.455 (0.003)	15.8 (0.6)
Unsubstituted	CH_3SOCH_3	3.733 (0.008)	1.9 (0.9)
3-*i*-Pr[c]	CH_3SOCH_3	3.828 (0.007)	4.0 (0.7)

[a] Refered to internal tetramethylsilane. [b] Estimated standard deviations of coefficients given in parentheses. [c] Chemical shift of 6 proton *cis* to isopropyl group.

V-6040 variable-temperature accessory; each spectrum was side band calibrated. Chemical shift measurements at 8 to 14 different temperatures were made for each piperazinedione in each solvent. Probe temperatures were determined using Varian samples of methanol and ethylene glycol with the Varian calibrations. Sample concentration was about 0.25 M in each solvent. Spectra were also obtained at 0.04 M for the nitro compound in dimethyl sulfoxide and hexafluoroacetone sesquideuterate, at *ca.* 30°, using a Varian C-1024 time-averaging computer to improve the signal-to-noise ratio. No differences in chemical shifts from the higher concentration were detected. Tetramethylsilane was the internal reference throughout.

For the variable-temperature studies, the amide protons (positions 1 and 4) of the piperazinediones were replaced by deuterium to reduce spin–spin splitting of the α-proton (3 and 6) lines. Each piperazinedione was dissolved in dry dimethyl-

TABLE II

STABILITY OF FOLDED CONFORMATION OF *para*-SUBSTITUTED 3-BENZYL-2,5-PIPERAZINEDIONES

Solvent	Substituent	$K_{25°}$[a]	$\Delta H°$, kcal/mol	ΔS, cal/(°K mol)	$\Delta\delta$,[b] ppm	Std dev, %[c]
CD_3SOCD_3	NO_2	4.8	−2.7	−5.8	0.72	3.6
	H	3.7	−2.8	−6.7	1.32	1.2
	OCH_3	2.6	−2.2	−5.5	1.38	2.0
	OH[d]	3.2	−2.6	−6.5	1.45	1.1
$CF_3COCF_3\cdot 1.5D_2O$	NO_2	4.6	−3.2	−7.7	0.93	3.8
	H	3.8	−3.2	−8.2	1.50	4.2
	OCH_3	3.3	−2.7	−6.6	1.45	3.3
CD_3COOD	NO_2	4.2	−2.6	−5.8	0.85	4.1
	H	2.8	−2.4	−5.9	1.64	2.9
	OCH_3	5.0	−3.1	−7.1	1.37	2.1
CF_3COOD	NO_2	3.1	−2.2	−5.1	0.79	2.4
	H	2.4	−2.3	−5.9	1.92	2.9
	OCH_3	5.1	−3.2	−7.6	1.32	2.0
	OH[d]	4.2	−3.2	−7.8	1.43	1.6

[a] [Folded conformation]/[all unfolded conformations]. [b] Calculated upfield shift of higher field glycyl α proton, relative to reference proton, when molecule is entirely in folded form. [c] Standard deviation of slope of computer-fitted van't Hoff plot. [d] Data of ref 2.

alanine), have been shown to favor, by 2–5 kcal/mol, the side-chain rotamer that brings the aromatic and the diketopiperazine rings into face-to-face proximity. The attraction between rings that stabilizes this folded conformation is not significantly dependent on solvent, and it has been suggested that it is chiefly one between amide dipoles and dipoles induced in the aromatic π electron cloud.[2] However, it is possible that there is a component of π–π donor–acceptor interaction in the stabilization. Therefore, we have carried out an nmr study, in the same manner as those earlier reported,[2,3] to seek a relationship between the π-electron density of the aromatic ring and the strength of the interaction favoring the folded conformation. The chemical shifts of the *cis* 6 protons of 3-(*p*-methoxybenzyl)-, 3-(*p*-nitrobenzyl)-, and 3-benzylpiperazine-2,5-diones were measured relative to corresponding protons of piperazine-2,5-diones lacking an aromatic ring. The temperature dependences of these differences were used to estimate the enthalpy of stabilization of the folded conformation and the extent to which the *cis* 6 proton is shielded in that conformation. Measurements were made in dimethyl sulfoxide, trifluoroacetic acid, and two solvents that have not been used in this work before, hexafluoroacetone sesquideuterate and acetic acid.

Experimental Section

Spectra and Calculations.—Proton magnetic resonance spectra were measured using a Varian A-60 spectrometer equipped with a

formamide and mixed with deuterium oxide; the mixed solvent was evaporated under vacuum and the process was repeated before the final solvent was added. All samples were sealed under vacuum.

The calculation of folded-form stabilization from the upfield shift of glycyl residue α protons has already been described.[2,3] For solutions in dimethyl sulfoxide, in which substituted piperazinediones are probably nonplanar,[3] the reference proton for determining the upfield shift in the benzyl piperazinediones was the *cis* 6 proton of 3-isopropyl-2,5-piperazinedione. For the other solvents, the protons of unsubstituted 2,5-piperazinedione served as reference. Linear least squares fits to the chemical-shift observations of the reference protons are given in Table I.

Materials.—The solvents used for the nmr studies were obtained commercially and used without modification. Two new piperazinediones were prepared as described below. L-3-benzyl-2,5-piperazinedione was prepared from glycyl-L-phenylalanine by a method previously described.[4] Recrystallized from ethanol–water, it had mp 270–271° (lit. mp 265.5°).[5]

L-3-*p*-Methoxybenzyl-2,5-piperazinedione.—To a suspension of cycloglycyl-L-tyrosyl[4,6] (0.44 g) in 20 ml of absolute ethanol was added 4.4 ml of 0.5 N sodium ethoxide in ethanol at 0°. The mixture was stirred for 1 hr at 0° and evaporated to dryness under vacuum. The residue was mixed with 15 ml of dry dimethylformamide and 0.32 g of methyl iodide; complete solution resulted, and the reacting mixture was stored overnight at room temperature. After removal of solvent under vacuum, the residue was crystallized from water, affording white needles of the methoxy compound, mp 246–247°, characterized by a singlet resonance for the methoxy protons at 3.76 ppm (in dimethyl sulfoxide-d_6).

Anal. Calcd for $C_{12}H_{14}N_2O_3$: C, 61.52; H, 6.02; N, 11.96. Found: C, 61.32; H, 5.97; N, 11.88.

DL-3-*p*-Nitrobenzyl-2,5-piperazinedione.—This substance was

(2) K. D. Kopple and D. H. Marr, *J. Amer. Chem. Soc.*, **89**, 6193 (1967).
(3) K. D. Kopple and M. Ohnishi, *ibid.*, **91**, 962 (1969).
(4) K. D. Kopple and H. G. Ghazarian, *J. Org. Chem.*, **33**, 862 (1968).
(5) E. Fischer and W. Schoeller, *Ann.*, **357**, 22 (1907).
(6) E. Fischer and W. Schrauth, *ibid.*, **354**, 28 (1907).

prepared from DL-*p*-nitrophenylalanine (Cyclo Chemical Corp.) *via* N-chloroacetylation, ammonolysis, and fusion of the resulting glycyl-*p*-nitrophenylalanine in phenol.[4] Glycyl-*p*-nitrophenylalanine, crystallized from water, decomposed above 290°.

Anal. Calcd for $C_{11}H_{13}N_3O_5$: C, 49.43; H, 4.90; N, 15.73. Found: C, 49.31; H, 4.89; N, 15.75.

3-*p*-Nitrobenzyl-2,5-piperazinedione, also crystallized from water, was obtained as pale yellow needles, mp 300° dec.

Anal. Calcd for $C_{11}H_{11}N_3O_4$: C, 53.01; H, 4.45; N, 16.86. Found: C, 52.91; H, 4.39; N, 17.03.

Results

The estimated enthalpies by which the folded form of the 3-benzylpiperazine-2,5-diones are stabilized are shown in Table II. In each of the four solvents, the enthalpies for the nitro and unsubstituted compounds are almost identical, and the estimated equilibrium constants, [folded]/[unfolded], do not differ by as much as a factor of 2. If the aromatic ring were acting as a donor of electron density in a donor–acceptor or charge-transfer complex, nitro substitution should destabilize the folded conformation;[7,8] if the aromatic ring were the acceptor, nitro substitution should increase the stability of the folded form.[9] Since neither effect is apparent, we think that it is safe to conclude that donor–acceptor interactions are not a major factor in stabilizing the face-to-face arrangement of rings in 3-benzylpiperidine-2,5-diones.

Two other features of the data in Table II should be noted.

In trifluoroacetic acid, stabilization of the folded form of the methoxy and hydroxy compounds is increased by 1 kcal/mol relative to the nitro and unsubstituted cases. There is an almost compensating increase in negative entropy for the folded form. This may indicate specific solvation, involving the oxygen substituents, of the folded form.

If the folded conformation of a given piperazinedione is the same in all solvents, the magnetic effect of the phenyl ring on the 6 proton will also be the same. There is no apparent interference to solvation at the periphery of the piperazinedione ring, and if there are no specific effects of solvation of the substituents on the aromatic ring, changes in $\Delta\delta$ with change in solvent reflect the exclusion of solvent from the face of the piperazinedione ring in the folded form. In this light, it is of interest that the limiting upfield shifts for the *cis* 6 protons of unsubstituted 3-benzylpiperazine-2,5-dione increase significantly with proton acidity of the solvent. An explanation of this trend in terms of the details of solvation will have to be deferred.

Registry No.—2,5-Piperazinedione, 106-57-0; 3-isopropyl-2,5-piperazinedione, 14771-77-8; L-3-*p*-methoxybenzyl-2,5-piperazinedione, 21996-47-4; DL-3-*p*-nitrobenzyl-2,5-piperazinedione, 21996-48-5; glycyl-*p*-nitrophenylalanine, 21996-49-6; 3-benzyl-2,5-piperazinedione, 10125-07-2; 3-*p*-hydroxybenzyl-2,5-piperazinedione, 5625-49-0.

(7) L. J. Andres and R. M. Keefer [*J. Amer. Chem. Soc.*, **72**, 3113 (1950)] have reported that the formation constant for the complex of nitrobenzene with silver ion is 0.19 l./mol, while that for benzene is 2.4 l./mol.

(8) G. F. Crable and G. L. Kearns [*J. Chem. Phys.*, **66**, 436 (1962)] report ionization potentials of 8.83, 9.56, and 10.18 eV for anisole, benzene, and nitrobenzene, respectively. Ionization potentials should correlate with donor ability in charge-transfer complex formation.

(9) Numerical data for benzene and nitrobenzene as acceptors in complexes are not available, but the π-acid properties of polynitrobenzenes are well known. J. E. Lovelock [*Nature*, **189**, 729 (1961)] reports that the affinity of nitrobenzene for thermal electrons is about 10^6 that of benzene.

Further Studies on N-Acylamino Acid Esters of 4-(Methylthio)phenol

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A new amino acid carboxyl protecting group, the 4-(methylthio)phenyl ester (MTP), has been developed and suggested for use in peptide synthesis by this laboratory.[2] The attractive feature of this protective ester is its facile conversion without racemization[3] to the activated 4-(methylsulfonyl)phenyl ester (MSO_2P).[4] This method of synthesis has been used successfully for the preparation of an N-carbobenzoxy heptapeptide[5] and advantageously in the synthesis of an N,N′-dicarbobenzoxy-O-depsipeptide.[6]

The broad range of potential utility for the MTP ester for the preparation of polypeptides prompted an investigation of the actual scope of this method with respect to the stability of amino acids and commonly used protecting groups to the oxidation conditions employed to produce the MSO_2P activated esters. To this end, the N-protected amino acid MTP esters were easily prepared, in good yield, by condensing the N-protected amino acid with 4-(methylthio)phenol, using N,N′-dicyclohexylcarbodiimide (DCC)[7] (see Table I).

However, oxidation of the N-carbobenzoxy amino acid MTP esters of lysine, alanine, leucine, glycine, and glutamic acid with 30% hydrogen peroxide in glacial acetic acid for 12 hr at room temperature resulted in the corresponding MSO_2P activated esters, even in the presence of the N-trifluoroacetyl and *t*-butyl ester protecting groups. These conditions were found to be too drastic for the *t*-butyloxycarbonyl and O-*t*-butyl ether protecting groups as well as the indole nucleus of tryptophan. In order to circumvent these difficulties, new milder oxidation conditions were used: a solution of the N-protected amino acid MTP ester in dioxane was treated with 3 equiv of 85% *m*-chloroperoxybenzoic acid at room temperature for 4 hr. Under these reaction conditions, it was possible to oxidize a large number of N-carbobenzoxy amino acid MTP esters (see Table II) to their corresponding MSO_2P activated esters. Of these amino acids, it is worthy of note that the following sensitive residues were found to be stable to these conditions: the indole nucleus of tryptophan, the nitroguanidine moiety of arginine, and the primary amide of glutamine. Further, these new oxidation conditions allowed the activated MSO_2P ester to be formed in the presence of N-*t*-butoxycarbonyl, N-carbobenzoxy, and O-*t*-butyl ether protecting groups.

The utility of the MTP ester also depends to a great extent on the ease with which the N-protecting group

(1) To whom any correspondence should be sent.

(2) B. J. Johnson and P. M. Jacobs, *Chem. Commun.*, 73 (1968).

(3) B. J. Johnson and P. M. Jacobs, *J. Org. Chem.*, **33**, 4524 (1968).

(4) R. Schwyzer and P. Sieber, *Helv. Chim. Acta*, **41**, 2190 (1958). These authors have reported a few 4-(methylsulfonyl)phenyl esters prepared from 4-(methylsulfonyl)phenol through the diaryl sulfite method.

(5) B. J. Johnson and E. G. Trask, *J. Org. Chem.*, **33**, 4521 (1968).

(6) B. J. Johnson, *ibid.*, **34**, 1178 (1969).

(7) J. C. Sheehan and G. P. Hess, *J. Amer. Chem. Soc.*, **77**, 1067 (1955).