Experimental Section[6]

Compounds 6–9 have particularly offensive odors.

2-(2-Chloroallylthio)ethanethiol (6).—A solution was prepared from 375 ml of ethanol, 60 g (1.5 moles) of sodium hydroxide, and 141 g (1.5 moles) of ethanedithiol. The solution was stirred and cooled with an ice bath, and 111 g (1.0 mole) of 2,3-dichloropropene was added dropwise in 1 hr. Stirring was continued for 2 hr, and 90% of the ethanol was removed by distillation. The residue was allowed to cool, and 300 ml of water and 200 ml of ether were added. The phases were separated, and the aqueous phase was extracted twice with 100-ml portions of ether. The ether extracts were combined, washed with saturated sodium chloride solution, dried with magnesium sulfate, and distilled. Compound **6** (65 g, 38%) was collected at 85–100° (1 mm) and had n^{24}D 1.5645. The nmr spectrum consists of bands centered at 322 and 316 cps ($CH_2=$), a narrow band at 208 cps ($=C-CH_2$), a multiplet from 157 to 180 cps (SCH_2CH_2S), and a triplet ($J \approx 8.1$ cps) at 97 cps (SH).

Anal. Calcd for $C_5H_9ClS_2$: Cl, 21.00. Found: Cl, 21.09.

When 1 mole of ethanedithiol instead of 1.5 moles was used, the yield of **6** was only 27 g (16%).

3-(2-Chloroallylthio)propanethiol (7) was prepared from 1,3-propanedithiol and 2,3-dichloropropene following a procedure similar to that used for **6**. The yield was 49 g (27%), bp 100–108° (0.5 mm), n^{24}D 1.5481. The nmr spectrum consists of bands centered at 324 and 318 cps ($=CH_2$), a narrow band at 208 cps ($=CCH_2$), a multiplet from 182 to 158 cps (SCH_2-CCH_2S), an apparent quartet ($J_{ap} \approx 6.6$ cps) centered at 138 cps ($C-CH_2-C$), and a triplet ($J \approx 8.0$ cps) at 95 cps (SH).

Anal. Calcd for $C_6H_{11}ClS_2$: C, 39.44; H, 6.07; Cl, 19.40; S, 35.09. Found: C, 39.51; H, 5.94; Cl, 19.26; S, 34.88.

2-Methyl-5,6-dihydro-1,4-dithiin (8).—Of several procedures used, the following gave the best yield of **8**. To a stirred solution of 16.8 g (0.10 mole) of **6** and 20 ml of *t*-butyl alcohol at 75° was added dropwise in 2 hr a solution of 7.8 g (0.068 mole) of potassium *t*-butoxide and 60 ml of *t*-butyl alcohol. The reaction mixture was allowed to cool, and it was added to a mixture of 150 ml of water and 100 ml of ether. The phases were separated, and the aqueous solution was extracted twice with 70-ml portions of ether. The ether solutions were combined, dried with magnesium sulfate, and distilled to give 2.3 g (25%) of **8**, bp 73–74° (4 mm), n^{22}D 1.5972, λ_{max} 278 mμ (ϵ 3020), λ_{min} 256 mμ (ϵ 1380), λ 1600 cm^{-1} ($C=C$). The nmr spectrum consists of a quartet ($J \approx 1.5$ cps) at 318 cps ($=CH$), a multiplet at 187–157 cps (SCH_2CH_2S), and a doublet ($J \approx 1.5$ cps) at 104 cps (CH_3).

Anal. Calcd for $C_5H_8S_2$: C, 45.41; H, 6.10; S, 48.49. Found: C, 45.33; H, 6.13; S, 48.66.

Before the preceding procedure was carried out, a similar reaction was run in which 11.2 g (0.10 mole) of potassium *t*-butoxide was used and the time for addition was 5 hr. During this run, gas–liquid partition chromatograms were taken to follow the course of the reaction. After 70% of the theoretical amount of potassium *t*-butoxide had been added, the intensity of the elution band due to **8** decreased relative to the height of the elution band due to *t*-butyl alcohol. The yield of **8** was 1.3 g (10%).

2-Methyl-6,7-dihydro-5H-dithiepin (9).—Treatment of 12.8 g (0.07 mole) of **7** with 7.8 g (0.07 mole) of potassium *t*-butoxide as described for the preparation of **8** gave 1.2 g (12%) of **9**, bp 73–75° (0.5 mm), n^{26}D 1.5881, λ_{max} 285 mμ (ϵ 4800), λ_{min} 255 mμ (ϵ 935), λ 1590 cm^{-1} ($C=C$). The nmr spectrum consists of a quartet ($J \approx 1.3$ cps) at 308 cps ($=CH$), two apparent triplets, both with $J_{ap} \approx 6.0$ cps, at 186 and 188 cps (CH_2-CCH_2), an apparent quintet ($J_{ap} \approx 6.0$ cps) centered at 116 cps, and a doublet ($J \approx 1.4$ cps) at 101 cps (CH_3).

Anal. Calcd for $C_6H_{10}S_2$: C, 49.27; H, 6.89; S, 43.84. Found: C, 49.19; H, 6.82; S, 43.88.

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(6) Boiling points are uncorrected. Infrared spectra were obtained with a Beckman IR-4 spectrophotometer. Nmr spectra were determined of compounds as 20% solutions in carbon tetrachloride at 56.4 Mc with a Varian Associates HR-60 system equipped with electronic integrator and base-line stabilizer. Resonance frequencies in nmr spectra were determined relative to internal tetramethylsilane (TMS) using the side-band technique with a Packard CD-200 audiooscillator and are reported in cycles per second downfield from the TMS resonance. Ultraviolet spectra were obtained of ethanol solutions using a Cary Model 14 recording spectrophotometer. Gas–liquid partition chromatograms were obtained using a Loe Model 1 Chromat-O-Flex with a 0.25 in. × 6 ft column packed with Silicone No. 550 on firebrick. Microanalyses were performed by Mr. V. H. Tashinian, Berkeley, Calif.

Conformational Analysis. VII. The Conformational Preference of the Nitro and Carboethoxyl Groups[1,2]

ROBERT J. OUELLETTE AND GARY E. BOOTH

Department of Chemistry, The Ohio State University,
Columbus, Ohio 43210

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In previous work[3] in which the relative stabilities of some carbomethoxyl and nitro bicyclic compounds were examined, it was assumed that the nitro and carbomethoxyl groups are sterically equivalent in systems which do not contain other substituents with nonbonded electrons. While the assumption appeared to be reasonable, there exists no definite experimental verification of the equivalence of the two groups.

Whereas the carboethoxyl and carbomethoxyl groups has been investigated by several techniques,[4] the nitro group has been little investigated save for its bond angles and bond lengths.[5] The necessary 4-*t*-butylnitrocyclohexanes are known, but base equilibration has not been carried out.[6] The nmr resonance signal for the α-hydrogen of the *cis* and *trans* isomers are τ 5.57 and 5.77, respectively. The corresponding resonance for nitrocyclohexane occurs at τ 5.72.[7] On the basis of agreement with a calculated spectrum it has been concluded that the nitro group is completely equatorial in nitrocyclohexane,[7] although the previous work of Huitric was apparently overlooked. While the experimental results of two groups of workers should not be used to calculate the conformational preference of the nitro group, it appears that nitrocyclohexane exists to a small extent in the axial conformation. Indeed, from the available experimental values the conformational preference of the nitro group is in the order of magnitude anticipated. Recently it has been reported that the agreement between calculated and experimental spectra for nitrocyclohexane is actually due to mathematical errors.[8] The details of the preliminary report will be outlined later.[9] Utilizing band widths, the calculated conformational equilibrium constant of 5.7 ± 1.5 at 26° is that anticipated for the nitro group.

We now report the determination of the conformational preference of the nitro group by direct equilibration. The nmr method is limited as the $-\Delta G$ for the nitro group is approximately 1.0 kcal/mole and the 12-cps difference between equatorial and

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(1) Paper VI: R. J. Ouellette, K. Liptak, and G. E. Booth, *J. Org. Chem.*, **31**, 546 (1966).

(2) The authors acknowledge Grant No. 2410-A4 from The Petroleum Research Fund of The American Chemical Society in support of this research. A grant-in-aid from The Ohio State University is also acknowledged.

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(4) For references, see E. L. Eliel, N. L. Allinger, S. J. Argyal, and G. A. Morrison, "Conformational Analysis," John Wiley and Sons, Inc., New York, N. Y., 1965, p 441.

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axial α-protons is somewhat small for an accurate determination.

Results and Discussion

The *cis*- and *trans*-4-*t*-butylnitrocyclohexane were equilibrated using 0.001 *M* potassium *t*-butoxide in *t*-butyl alcohol. The concentration of substrate was approximately 0.03 *M*. Equilibrations were carried out at 50, 75, and 100° and the calculated equilibrium constants are tabulated in Table I. The enthalpy and entropy change for the axial–equatorial transformation is -0.98 ± 0.08 kcal/mole and 0.6 ± 0.2 cal/deg, respectively.

TABLE I

CONFORMATIONAL EQUILIBRIUM CONSTANTS[a]

Compound	Temp, °C	K^a
Nitrocyclohexane	50.0	6.28
	75.0	5.67
	100.0	5.12
Carboethoxycyclohexane	40.0	7.27
	60.0	6.55
	80.0	5.95
	100.0	5.48
	120.0	5.05
	140.0	4.75

[a] Equilibrium constants were reproducible to ±3% for the nitro compounds and ±2% for the carboethoxyl compounds.

The *cis*- and *trans*-4-*t*-butylcarboethoxycyclohexane were equilibrated using 0.10 *M* sodium ethoxide in ethanol. The substrate concentration was 0.03 *M*. Studies were carried out at 20° temperature intervals from 40 to 140°. The calculated equilibrium constants are tabulated in Table I and are in close agreement with those previously reported for the carboethoxyl group.[4] The enthalpy and entropy change for the axial–equatorial transformation is -1.09 ± 0.03 kcal/mole and 0.4 ± 0.1 cal/deg, respectively.

That the equilibrium constants for axial–equatorial conversions for the nitro and carboethoxyl groups are closely similar supports the assumptions previously made in our studies of bicyclic compounds.[3] Indeed, the near identity of the two groups is not surprising, as the conformational preference of substituents is usually governed by the number of substituents on the atom next to the ring rather than the type of substituents.

The question of conformational entropy differences have not been investigated extensively, although it would not be expected to be important for spherically symmetrical groups and groups of small van der Waals radii. Trigonally hybridized carbon or other groups having only two substituents attached to the atom immediately adjacent to the ring might be expected to exhibit some entropy contribution. Since the carboethoxyl group is not axially symmetrical, it would be expected to be more restricted in rotation when it is in the axial position than when it is in the equatorial position owing to repulsion between the oxygen atoms and the 3,5-*syn*-axial hydrogens. Therefore, the entropy change for axial–equatorial conversion would be expected to be positive.

The observed entropy changes for both the nitro and the carboethoxyl groups are such as to indicate that restricted rotation probably occurs in the axial position. The minimum energy conformation in the axial position is most likely the one in which the plane of the trigonal systems are parallel to the plane of the 3,5-*syn*-axial carbon–hydrogen bonds. An entropy contribution for the carbomethoxyl group has been calculated from a study of 5-alkyl-*cis*-1,3-disubstituted cyclohexanes. An entropy change of -0.5 cal/deg for the equatorial–axial conversion of the carbomethoxy group has been observed, although no significant entropy contribution was found for the isopropyl ester.[10] Thus, the present work on the carboethoxyl group is in agreement with that of Armitage, Kenner, and Robinson on the carbomethoxyl group.

An entropy contribution of -0.4 cal/deg to the axial–equatorial conversion for the methyl group has been observed.[11] However, the use of spirodiazirines as a method in conformational analysis may not be general. Additional experiments will be necessary to support the contention that distortion of the six-membered ring in the spirodiazirines is relatively minor. The entropy contribution for the cyano group in a *t*-butyl alcohol as solvent is approximately 0.7 cal/deg.[12] However, effect of solvent on the conformational preference of the cyano group has been examined[13] and solvation may contribute to the entropy term of the cyano group. The hydroxyl group apparently exhibits an anomalously high entropy contribution of 1.2 cal/deg.[14] This value is in distinct contrast to the recent equilibrium values[15] in which the entropy contribution is zero. The latter value appears more reasonable.

Additional data are needed in order to provide some rational basis for entropy contributions to the conformational preference of substituents. At the present time the entropy contributions appear to be real but do not contribute significantly to the conformational preference of substituents.

Experimental Section

The compounds utilized in this study have been described previously.[4,6] The analytical procedure for the determination of the equilibrium constants listed in Table I have been described in an earlier paper of this series.[3]

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Carbamoylphosphines

GRACE PETERS PAPP AND SHELDON A. BUCKLER

Chemical Department, Central Research Division,
American Cyanamid Company, Stamford, Connecticut

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The preparation of N-substituted carbamoylphosphines (**1**) from the reaction of aryl isocyanates and phosphines has been reported.[1-3] Cyanic acid generated

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