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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[10] B. J. Armitage, G. W. Kenner, and M. J. T. Robinson, *Tetrahedron Letters*, **No. 20**, 747 (1964).

[11] J. J. Uebel and J. G. Martin, *J. Am. Chem. Soc.*, **86**, 4618 (1964).

[12] B. Rickborn and F. R. Jensen, *J. Org. Chem.*, **27**, 4606 (1962).

[13] C. D. Ritchie and A. L. Pratt, *J. Am. Chem. Soc.*, **86**, 1571 (1964).

[14] J. Reisse, J. C. Celotti, D. Zimmerman, and G. Chiurdoglv, *Tetrahedron Letters*, 2145 (1964).

[15] E. L. Eliel and S. H. Schroeter, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 34S.

Carbamoylphosphines

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Received July 26, 1965

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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[1] S. A. Buckler, *J. Org. Chem.*, **24**, 1460 (1959).

[2] M. M. Rauhut and H. A. Currier, *ibid.*, **26**, 4628 (1961).

[3] S. A. Buckler and M. Epstein, *Tetrahedron*, **18**, 1221 (1962).

TABLE I

CARBAMOYLPHOSPHINES AND THEIR OXIDES

Product	M.p., °C.	Solvent	Yield, %	Calcd., %				Found, %			
				C	H	N	P	C	H	N	P
$(C_6H_{11})_2PCONH_2$	121–124	Crude[a]	80	64.48	10.03			64.07	9.93		
$(C_6H_{11})_2P(O)CONH_2$	177–179	C_6H_{14}–MeOH	...	60.68	9.40	5.44	12.04	60.36	9.61	5.55	12.19
$(C_6H_5)_2PCONH_2$	115–116	C_6H_{14}–C_6H_6	26[b]	68.12	5.28	6.11	13.52	68.04	5.59	5.9	13.45
$(C_6H_5)_2P(O)CONH_2$	190–191	C_6H_{14}–C_6H_6	15[b]	63.67	4.93	5.71		63.32	5.48	5.76	
$(NCCH_2CH_2)_2P(O)CONH_2$	179–180	MeOH	34	42.21	5.06	21.10	15.55	42.52	4.92	20.81	15.85
$(n\text{-}C_4H_9)_2P(O)CONH_2$	177–178	C_6H_6	34[c]	52.67	9.82	6.82		52.46	9.86	6.86	
$C_6H_5P(CONH_2)_2$	159–161	MeOH	14			14.28	15.78			14.47	15.75
$C_6H_{11}P(H)CONH_2$	Oil	Crude[a]	57[b]								
$C_6H_{11}P(H)(O)CONH_2$	157–159	*i*-PrOH	23[b]	47.99	8.06		17.68	47.79	8.03		17.30

[a] Characterized as the oxide. [b] The oxide and the phosphine were both isolated. [c] Nonaqueous addition.

in situ has been found to react similarly with primary and secondary phosphines (but not with phosphine itself) to form unsubstituted mono- and dicarbamoylphosphines (**2**). Reactivity of the carbamoylphosphines toward atmospheric oxygen varied with the

$$R_xPH_{3-x} + (3 - x)R'NCO \longrightarrow \underset{\mathbf{1}}{R_xP(CONHR')_{3-x}}$$

$$x = 0, 1, 2$$

$$R_xPH_{3-x} + (3 - x)HOCN \longrightarrow \underset{\mathbf{2}}{R_xP(CONH_2)_{3-x}} \xrightarrow{[O]} \underset{\mathbf{3}}{R_xP(O)(CONH_2)_{3-x}}$$

$$x = 1, 2$$

substituent: alkyl > aryl ≷ alicyclic. Alkyl derivatives, such as butyl and 2-cyanoethyl, were isolable only as oxides (**3**), while cyclohexyl and phenyl derivatives formed oxides upon attempted recrystallization or prolonged exposure to air.

Experimental Section

The liberation of cyanic acid from potassium cyanate can be conveniently effected in an aqueous or nonaqueous medium, as required by the water solubility of the phosphine product. In a typical preparation, a concentrated aqueous solution of 5.6 g. (0.07 mole) of potassium cyanate was added in 10 min. under nitrogen to a stirred solution of 7.0 g. (0.035 mole) of dicyclohexylphosphine in 40 g. (0.67 mole) of glacial acetic acid at 70–80°. Heating at reflux was continued until the evolution of cyanic acid ceased, after which the cooled mixture was poured into water to precipitate 6.7 g. (80%) of carbamoyldicyclohexylphosphine. (Additional product in the form of the oxide could be obtained by methanol extraction of the concentrated filtrate, after conversion of the acetate salts present to sulfates with sulfuric acid.) Infrared and elemental analyses of the crude material were satisfactory, but attempted recrystallization from hexane–methanol converted it to the oxide. Reverse addition of excess acetic acid to an acetonitrile slurry of a phosphine and freshly ground potassium cyanate was substituted when the product was appreciably water soluble, as was carbamoyldi-*n*-butylphosphine (Table I).

Completeness of the reaction could be determined by following the reduction or elimination of the P–H absorption and the corresponding appearance of P–CO–NH₂ bands in the infrared spectrum of the products. (Aliphatic and aromatic primary and secondary phosphines absorb at 2320–2275 cm.$^{-1}$.) The P–CO–NH₂ group has infrared bands similar to those of the group C–CO–NH₂, with absorption at 3400–3150 (usually a doublet), NH₂ stretch; 1670–1630, C=O stretch; and 1615–1590 cm.$^{-1}$, NH₂ deformation, when run as a Nujol mull.[4]

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[4] We are grateful to Mr. N. B. Colthup for the spectral assignments.

1,4- and 3,4-Cycloaddition Reactions of 1,1-Diphenyl-1,3-butadiene with Tetracyanoethylene

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Received July 30, 1965

Current interest in organometallic additions to conjugated dienes and in the allylic rearrangements of the resulting organometallic systems has prompted us to examine the behavior of 1,1-diphenyl-1,3-butadiene (II) toward other electrophilic addends as well. The finding that diisobutylaluminum hydride adds to II in a 3,4 fashion and that the resulting adduct then rearranges to a 1,4 adduct[2] suggested that other electrophiles might show a similar behavior. In the present study the interaction of 1,1-diphenyl-1,3-butadiene with the potent electrophile, tetracyanoethylene (TCNE), was investigated.

From the experience of other workers, one might expect TCNE to add to II in a 1,2[3] or 3,4 fashion,[4] a 1,4 Diels–Alder fashion,[5] or possibly a Diels–Alder reaction involving the *ortho* positions of the phenyl groups and the 1,2-olefinic linkage.[6] Furthermore, a recent report published during the course of this study reveals that with 4-methyl-1,3-pentadiene 1,2 and 1,4 additions of TCNE can result concurrently.[7] Despite subsequent examination of more than a dozen other dienes, only the normal 1,4 addition of TCNE was observed.[8] Such competing 1,2 and 1,4 additions to dienes are of potential interest in elucidating the detailed mechanism of the Diels–Alder reaction.[8] Of additional value would be a diene system which

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[2] J. J. Eisch and G. R. Husk, *J. Organometal. Chem.*, **4**, 415 (1965).

[3] J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Am. Chem. Soc.*, **84**, 2210 (1962).

[4] A. T. Blomquist and Y. C. Meinwald, *ibid.*, **81**, 667 (1959).

[5] W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *ibid.*, **80**, 2783 (1958).

[6] T. Wagner-Jauregg, *Ann.*, **491**, 1 (1931); W. J. Middleton, *J. Org. Chem.*, **30**, 1390 (1965).

[7] C. A. Stewart, Jr., *J. Am. Chem. Soc.*, **84**, 117 (1962).

[8] C. A. Stewart, Jr., *J. Org. Chem.*, **28**, 3320 (1963).