(b.p. 30–60°). Fractions 5–8 contained essentially pure compound 18 for a total of 3.45 g. (37%). After two recrystallizations from petroleum ether (b.p. 30–60°), the 4,4 - dimethyl - 6 - (2 - hydroxy - 2 - propyl) - 1 - phenylcyclohexene melted at 66–66.5°; infrared spectrum (CCl_4), 2.82 μ (m) and 2.92 μ (w).

Anal. Calcd. for $C_{17}H_{20}O$: C, 83.55; H, 9.90. Found: C, 83.35; H, 10.00.

***trans*-4-*tert*-Butyl-6-nitro-1-*p*-tolylcyclohexene (Compound 23).**—4-*tert*-Butyl-1-*p*-tolylcyclohexene, 6.84 g. (0.03 mole), was nitrated[5] using 2.6 g. (0.04 mole) of 70% nitric acid, 100 ml. of acetic anhydride, and 5 drops of sulfuric acid. The crude reaction product, after hydrolysis of the acetic anhydride and extraction with ether, was chromatographed on a 3 × 70 cm. silica gel column packed in 1% ether–petroleum ether (b.p. 60–70°). Elution with 4500 ml. of 1% and 2800 ml. of 5% ether–petroleum ether solutions afforded, as the only solid material, 1.83 g. of 1-acetoxy-*cis-tert*-butyl-*trans*-2-nitro-1-*p*-tolylcyclohexane, m.p. 124–128.5°. Two recrystallizations from petroleum ether raised the melting point to 131.5–132.5°; infrared spectrum ($CHCl_3$), 8.50 (s), 9.15 (m), 10.32 (m), and 11.02 (w) μ. The infrared spectrum is consistent with the assigned configuration.[5]

Anal. Calcd. for $C_{19}H_{27}NO_4$: C, 68.44; H, 8.16; N, 4.20. Found: C, 68.56; H, 8.13; N, 4.45.

A portion (0.50 g.) of the β-nitroacetate was treated with 15 ml. of acetic anhydride containing 15 drops of sulfuric acid.[5] The resulting solution was left for 10 min. at room temperature and then poured into an excess of water. After hydrolysis of the acetic anhydride was complete, the solid was collected by filtration and weighed 0.41 g., m.p. 67–70°. After one recrystallization from petroleum ether (b.p. 30–60°), the *trans*-4-*tert*-butyl-6-nitro-1-*p*-tolylcyclohexene melted at 73–75°. Two further recrystallizations raised the melting point to 75–76°; infrared spectrum ($CHCl_3$), 6.42 μ (s). Once, a solid form melting at 61–63°, resolidifying at this temperature and then melting again at 75–76° was obtained.

Anal. Calcd. for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.13; H, 8.74; N, 5.34.

1-(1-Cyclohexenyl)cyclohexene (Compound 28).—The procedure of Gruber and Adams[30] was followed. The diene obtained boiled at 81.5° (2.0 mm.), n^{25}_D 1.5321; reported[30] n^{20}_D 1.5322. It was 94% pure by GLC.

In Table II are listed the retention volumes (GLC) for a number of 1-arylcyclohexenes relative to 1-phenylcyclohexene. Comparable relationships between V_R and structure have been reported for alkylated biphenyls with regard to noncoplanarity of the conjugated systems.[31]

TABLE II
RETENTION VOLUMES OF 1-ARYLCYCLOHEXENES RELATIVE TO 1-PHENYLCYCLOHEXENE[a]

Compound	V_R/V_R 1-phenylcyclohexene
1-Methyl-2-phenylcyclohexene	0.91
1-*o*-Tolylcyclohexene	1.04
6-Methyl-1-phenylcyclohexene	1.05
4-Methyl-1-phenylcyclohexene	1.24
1-*p*-Tolylcyclohexene	1.49
6,6-Dimethyl-1-phenylcyclohexene	1.08
4,4-Dimethyl-1-phenylcyclohexene	1.34
1-(2,6-Dimethylphenyl)cyclohexene	1.35
1-Isopropyl-2-phenylcyclohexene	1.25
6-Isopropyl-1-phenylcyclohexene	1.67
6-*tert*-Butyl-1-phenylcyclohexene	2.27
6,6-Dimethyl-1-phenylcyclohexene	2.3
4-*tert*-Butyl-1-phenylcyclohexene	3.52

[a] A Perkin-Elmer Vapor Fractometer fitted with a 6-ft. silicone oil DC-200 column was employed. The column temperature was 200° and the helium pressure was 20 p.s.i.

Acknowledgment.—The author is indebted to Dr. W. B. Schwabacher for determining the n.m.r. spectra. The author wishes to thank the National Science Foundation for a postdoctoral fellowship, and Professor M. M. Kreevoy for reading the rough manuscript.

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[30] E. E. Gruber and R. Adams, *J. Am. Chem. Soc.*, **57**, 2555 (1935).

[31] E. A. Johnson, "Steric Effects in Conjugated Systems," Academic Press, Inc., New York, N. Y., 1958, pp. 174 ff.

Conformations. II. Proton Magnetic Resonance Determination of C-6 Substituent Conformations in 6-Substituted 1-Phenylcyclohexenes

EDGAR W. GARBISCH, JR.[1]

School of Chemistry, University of Minnesota, Minneapolis 14, Minnesota

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Preferred conformations for C-6 substituents in a number of 6-substituted 1-phenyl(and methyl)cyclohexenes have been determined from the widths at half height of the C-6 proton magnetic resonance bands. Bulky substituents, *e.g.*, 6-*tert*-butyl, were found to be primarily axial. Olefinic proton and C-6 proton coupling constants, extracted from the respective absorptions in a number of instances, were used to approximate dihedral angles between adjacent protons.

Conformations of cyclohexene derivatives have not been widely investigated.[2] Sakashita has concluded recently[3] from infrared and Raman spectra that *axial*-3-halo- and *axial*-4-halocyclohexenes are more stable in the liquid state than their equatorial counterparts. The chair conformation of cyclohexene has been estimated[4] to be favored over the boat form by about 2.7 kcal./mole, and this conformational preference has experimental support for a number of derivatives.[2]

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[1] (a) N.S.F. Postdoctoral Fellow, 1961–1962. (b) Paper I in this series, *J. Org. Chem.*, **27**, 4243 (1962). (c) Present address: Department of Chemistry, University of Chicago, Chicago 37, Illinois.

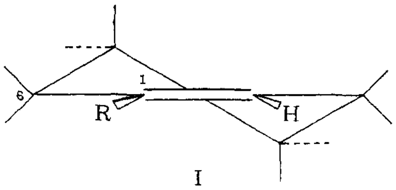
[2] W. Klyne, "Progress in Stereochemistry," Vol. I, Academic Press Inc., New York, N. Y., 1954, pp. 81 ff.

[3] K. Sakashita, *Nippon Kagaku Zasshi*, **81**, 49 (1960); *ibid.*, **80**, 972 (1959); *Chem. Abstr.*, **54**, 2008h, 12015b (1960).

[4] C. W. Beckett, N. K. Freeman, and K. S. Pitzer, *J. Am. Chem. Soc.*, **70**, 4227 (1948).

Proton magnetic resonance has proved useful for determinations of conformations in saturated six-membered ring derivatives.[5–8] Axial protons have been shown to exhibit shielding values at higher magnetic fields as compared with equatorial protons[5]; however, the difference between the representative signals is not always large[5] and exceptions have been reported.[5b] Conformational analysis has been treated in a quantitative manner utilizing chemical shifts as a basis for analysis.[6] Karplus[9] has related the magnitude of coupling constants between protons on adjacent carbon atoms to the dihedral angles between the protons, and this work provides theory for the observations that, for six-membered rings, coupling between adjacent axial protons is generally about two to three times as large as between adjacent equatorial protons which, in turn, is of about the same order of magnitude as between axial and equatorial protons.[5] Often resolution of absorption bands is inadequate for the determination of coupling constants, and for these instances the width at half height (W_H) of the appropriate absorption band has been shown to be valuable for the assignment of preferred conformations.[5,7,8,10] For compounds which are not rigid, W_H (and J) values from coupling between protons on adjacent carbon atoms should approximate time-weighted averages from the conformations present provided interconversion is rapid.[10,11] Provided W_H of appropriate proton absorptions are available from conformationally homogeneous reference compounds, qualitative evaluations of the substituent conformations in compounds with comparable proton interactions should be possible.

It is the purpose here to derive the preferred conformations of C-6 substituents from the W_H of the C-6 proton resonance for a number of 6-substituted 1-phenyl(and methyl)cyclohexenes (see Table I). The coupling involved between the C-6 and C-5 protons is of the AXY type[12] with A equal to the C-6 proton (see I).



I

The widths at half height of the C-1 proton magnetic resonance of *cis-* and *trans*-4-*tert*-butylcyclohexanol have been reported to be 7 c.p.s.[5a,10] and 22 c.p.s.[5a] and 18.5 c.p.s.,[10] respectively. The W_H of the C-2 proton absorption of 10-methyl-*trans*-decal-*trans-* and *cis*-2-ol are 6.7 c.p.s. (equatorial proton) and 19.5 c.p.s. (axial proton), respectively.[10] These compounds are assumed conformationally homogeneous, and are thought to represent reasonable models for the C-6 proton couplings of the 6-substituted 1-phenyl(and methyl)-cyclohexenes. Correlations with these models can, at best, be only qualitative, since: (1) the allylic protons of cyclohexene are thought to be quasi-axial and quasi-equatorial[13] (2) deformations of the ring as a result of substitution will alter dihedral angles and consequently lead to variances of coupling constants and band widths, (3) the appropriate absorption bands of the models represent AX^2Y^2 or AX^4 systems and would be expected to exhibit somewhat larger W_H than those of the AXY system involved here (long range coupling[12] between C-2-H and C-6-H, however, will serve to broaden the C-6 proton bond), and (4) coupling constants will vary slightly depending upon the electronegativity of the group(s) present.[11b]

In Table I are listed a number of 1-phenylcyclohexene and several 1-methylcyclohexene derivatives with preferred conformations of the C-6 substituents. For C-6 proton bands exhibiting widths at half height between 13 and 15 c.p.s., there is considered to be no preference of the C-6 substituent for either an axial or an equatorial conformation. The C-6 substituent is considered to have preference for the equatorial position for W_H of C-6 proton bands >15 c.p.s., and to have preference for the axial position for W_H of C-6 proton bands <13 c.p.s.

It is apparent from Table I that conformations of C-6 substituents in 6-substituted 1-phenyl(or methyl)cyclohexenes are in opposition to normal conformational trends for substituted cyclohexanes. Most striking is the conclusion that *tert*-butyl and 2-hydroxy-2-propyl functions substituted on C-6 of 1-phenylcyclohexene largely prefer the axial conformation. The W_H of 14 c.p.s. for the C-6 proton absorption of 4,4-dimethyl-1-phenylcyclohexene (compound 1) represents that anticipated for a C-6 substituent with no conformational preference. The C-6 substituents of 4,4-dimethyl-6-substituted 1-phenylcyclohexenes (compound 5, 7, and 13) are shown to be largely in the equatorial conformation. This result was anticipated in light of the recently determined energy of 3.7 kcal./mole for a 1,3-diaxial dimethyl interaction in cyclohexane.[14] Also, methyl interactions have been shown[15] to restrict bromine to the equatorial position in 4,4-dimethyl-2-bro-

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[5] (a) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 6098 (1958). (b) K. J. Williamson and W. J. Johnson, *ibid.*, **83**, 4623 (1961).

[6] L. W. Reeves and K. O. Stromme, *Trans. Faraday Soc.*, **57**, 390 (1961); E. L. Eliel, *Chem. Ind.* (London), 568 (1959); E. L. Eliel and M. H. Gianni, *Tetrahedron Letters*, 97 (1962).

[7] S. Brownstein and R. Miller, *J. Org. Chem.*, **24**, 1886 (1959).

[8] A. C. Huitric and J. B. Carr, *ibid.*, **26**, 2648 (1961).

[9] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

[10] J. I. Musher, *J. Am. Chem. Soc.*, **83**, 1146 (1961).

[11] (a) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chap. 13; (b) F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 747 (1962), and A. A. Bothner-By and C. Naar-Colin, *ibid.*, **84**, 743 (1962).

[12] The long range coupling (*ca.* 1 c.p.s.) between C-6-H and C-2-H which is now under investigation is not considered here.

[13] D. H. R. Barton, R. C. Cookson, W. Klyne, and C. W. Shoppe, *Chem. Ind.* (London), 21 (1954).

[14] N. L. Allinger and M. A. Miller, *J. Am. Chem. Soc.*, **83**, 2145 (1961).

[15] E. J. Corey, *ibid.*, **75**, 3297 (1953).

TABLE I

PREFERRED CONFORMATIONS OF C-6 SUBSTITUENTS OF C-6 SUBSTITUTED 1-PHENYL(OR METHYL)CYCLOHEXENES (I)[a]

Compound no.	C-1 substituent	C-2-olefinic-H J c.p.s.[e] (τ)	C-4 substituents	C-6 substituent (C_6H, τ)	W_H of C-6—H (c.p.s.)	Preferred conformation of C-6 substituent
1	Ph	8[i] (4.04)	CH_3,CH_3	H (7.63)	14	[b]
2	Ph	4.1 (4.25)	H,H	*tert*-Butyl (7.38)	10.5[c]	ax
3	Ph	4.0 (3.71)	H,H	Ph (6.08)	10.5	ax
4	Ph	3.8 (4.14)	H,H	$(CH_3)_2COH$ (7.18)	9	ax
5	Ph	4.1 (4.34)	CH_3,CH_3	$(CH_3)_2COH$ (7.12)	21 (J = 8.6 c.p.s.)[d]	eq
6	Ph	*ca.* 4 (3.89)	H,H	$COCH_3$ (6.405)	13.5	[j]
7	Ph	9[i] (3.95)	CH_3,CH_3	$COCH_3$ (6.37)	22	eq
8	CH_3	(4.42)	H,H	$COCH_3$ (7.045)	14	[j]
9	Ph	3.8 (3.66)	H,H	NO_2 (4.565)	9[c]	ax
10	*p*-CH_3—C_6H_4	2.4 and 4.8[f] (3.64)	*tert*-Butyl, H	*trans*-NO_2 (4.57)	8	ax
11	Ph	2.25 and 4.5[g] (3.63)	CH_3,H	*trans*-NO_2 (4.57)	8	ax
12	Ph	9[i] (3.86)	CH_3,H	*cis*-NO_2 (4.33)	19	eq
13	Ph	3.6 (3.88)	CH_3,CH_3	NO_2 (4.42)	21 (J = 8.4 c.p.s.)[d]	eq
14	CH_3	(4.17)	H,H	NO_2 (5.20)	12	ax
15[h]	CH_3	(NO_2)[h]	H,H	Br (5.30)	8[h]	ax[h]

[a] In CCl_4 at *ca.* 20°. Tau values have a mean deviation of less than ±0.02 p.p.m. and were measured from the midpoints of the absorptions. W_H and J values have a mean deviation of ±1 c.p.s. and ±0.3 c.p.s., respectively. [b] The C-6 protons are considered magnetically equivalent. [c] Partially resolved triplet in some traces. [d] Taken from a trace with a sufficiently resolved band. Apparent 1:2:1 triplet. [e] 1:2:1 triplet. [f] Four lines with equal spacings of 2.4 c.p.s. and equal intensities. [g] Four lines with equal spacings of 2.25 c.p.s. and equal intensities. [h] 6-Bromo-1-methyl-2-nitrocyclohexene. The n.m.r. spectrum was taken of a mixture of 6-bromo-1-methyl-2-nitrocyclohexene (59%) and 6-bromo-1-methyl-6-nitrocyclohexene (41%). The olefinic proton in the latter compound has a tau value of 4.18. [i] Width at half height (W_H). [j] No conformational preference.

mocyclohexanone. The configurations of compounds 10–12 have been resonably established by other methods.[16] The preferred conformations determined for these compounds, while being anticipated, add additional support to the configurations assigned.[16]

It is evident that many groups on C-6 of 1-phenylcyclohexene are confined largely to axial conformations. It is concluded that C-6 equatorial substituents in these compounds are held more nearly in the plane subscribed by C-2–C-1–C-6 than are axial C-6 substituents; interaction between equatorial substituent and aryl being, at least in part, the impetus for the axial conformations observed. The hypsochromic shifts of about 3 mμ observed in the ultraviolet spectra[1b] for equatorial C-6 nitro and 2-hydroxy-2-propyl as compared with the axial derivatives (compounds 4 and 5, and 9–13 in Table I) serve to support this conclusion.

The significant difference in the conformational preferences for 6-nitro- and 6-acetyl-1-phenylcyclohexene was not expected (acetyl shows little conformational preference, whereas nitro is confined largely to an axial conformation). The difference is not as pronounced for the analogously substituted 1-methylcyclohexenes.[17] These differences are thought to suggest that the nitro group is of larger effective bulk than the acetyl group. This interpretation will be further substantiated and discussed in paper III.

For 6-nitro-1-phenylcyclohexene (compound 9), a semiquantitative determination of the conformational preference of the nitro function is possible by utilizing the olefinic proton chemical shifts. These shifts are due to variances in the benzene ring conformation and will be discussed in paper III. The shielding value for the olefinic proton of 4-methyl-1-phenylcyclohexene (4.01 τ)[1b] is essentially the same as that for the olefinic proton of 1-phenylcyclohexene (4.00 τ)[1b]; therefore, taking compounds 11 and 12 as being conformationally homogeneous, $\Delta\tau_{\text{olefinic-H}}$ for C-6—H_a and C-6—H_e is 0.23 p.p.m. The $\Delta\tau$ for the C-6—H of 6-nitro-1-phenylcyclohexene and C-6—H_e of compound, 12 is 0.20 p.p.m. The nitro function in 6-nitro-1-phenylcyclohexene is then found to be about 90% axial and 10% equatorial. Using the respective W_H values for the C-6 protons of these compounds, comparable conformations are calculated. This is in good agreement with equilibrium studies on *cis*- and *trans*-4-*tert*-butyl-6-nitro-1-phenylcyclohexene.[17]

The olefinic proton magnetic resonance of *trans*-4-*tert*-butyl-6-nitro-1-*p*-tolylcyclohexene (compound

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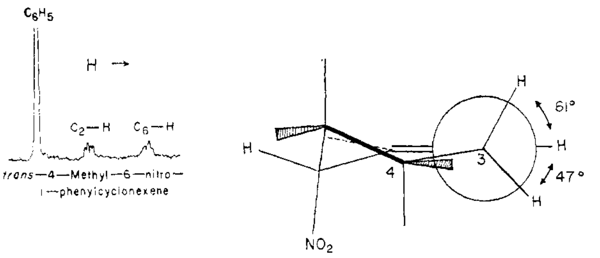
(16) E. W. Garbisch, Jr., Ph.D. thesis, Northwestern University, 1961. This work will be published shortly. Compound 10 was prepared in the same manner as described for *trans*-4-*tert*-butyl-1-phenylcyclohexene.

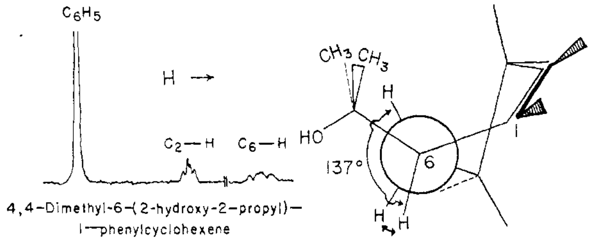
(17) The conformational preference for axial nitro in 6-nitro-1-phenylcyclohexene, as determined above, is supported by the observation[16] that base-catalyzed equilibration of the *cis*- and *trans*-4-*tert*-butyl-6-nitro-1-phenylcyclohexenes led to an equilibrium composition of 85 to 95% *trans* stereoisomer (axial nitro). Synthesis of *cis*- and *trans*-4-*tert*-butyl (or methyl)-6-acetyl-1-phenylcyclohexene has so far been impeded by unsuccessful attempts to separate the stereoisomers.

10) and *trans*-4-methyl-6-nitro-1-phenylcyclohexene (compound 11) appear as four lines with equal spacings of 2.4 c.p.s. and 2.25 c.p.s., respectively, and with equal intensities (AXY-type with A equal to the olefinic proton). This gives approximate J_{AY} J_{AX} values[5,12,18] of 2.4 c.p.s. and 4.8 c.p.s., respectively for compound 10, and 2.25 c.p.s. and 4.5 c.p.s., respectively for compound 11. From these splittings, dihedral angles of about 61° (J_A = 2.4–2.25 c.p.s.) between C-3—H_a and C-2—H, and about 47° (J_{AX} = 3.8–4.5 c.p.s.) between C-3—H_e and C-2—H (see II, Fig. 1) are estimated using the revised expression of Karplus's equation[9] as given by Williamson and Johnson.[5b] Corey's and Sneen's model for cyclohexene[19] predicts dihedral angles of about 68° and 39° for C-3—H_a, C-2—H and C-3—H_e, C-2—H, respectively. The C-6 proton resonance for compounds 5 and 13 is a 1:2:1 triplet with J = 8.6 c.p.s. and 8.4 c.p.s., respectively. If this is taken to mean that $J_{AX} \cong J_{AY}$,[18] dihedral angles between C-6—H_a and C-5—H_e are about 22°, and dihedral angles between C-6—H_a and C-5—H_a are approximately 137° for both compounds (see III, Fig. 2). The angles shown in II and III are consistent with the quasi-axial and quasi-equatorial concept for the allylic protons in cyclohexene.[13]



II

Fig. 1



III

Fig. 2

The olefinic proton resonance was resolved for a number of compounds into a 1:2:1 triplet with splittings ranging from 3.6 to 4.1 c.p.s. (see Table I). Should $J_{AX} \cong J_{AY}$ in these instances, this would mean that angles C-3—H_a, C-2—H $\cong$ angles C-3—H_e, C-2—H $\cong$ 53° ($J \cong$ 3.6 c.p.s.) to 50° (J = 4.1 c.p.s.); see II.[20]

No definite conclusion regarding possible cyclohexene ring deformations can be drawn from the data presented in this work. The larger tau value of 4.42 for the axial C-6 proton absorption of 4,4-dimethyl-6-nitro-1-phenylcyclohexene as compared with 4.33 for the axial C-6 proton absorption of *cis*-4-methyl-6-nitro-1-phenylcyclohexene (compounds 28 and 27, respectively) may be evidence that the chair-like conformation of the cyclohexene ring is intact in these instances. The axial C-4 methyl is calculated[21] to shield the C-6 axial proton by approximately 0.14 p.p.m. (0.09 p.p.m. is found). This shielding would be largely reduced, if not reversed, if the conformation of the ring was primarily boat (by model inspection).

Experimental

The 1-phenylcyclohexene derivatives discussed in this paper, together with proton magnetic resonance and ultraviolet spectra data have been reported in paper I of this series.[1b] 1-Methyl-6-nitrocyclohexene was prepared as described by Bordwell and Garbisch.[22] The n.m.r. spectra of the 1-methylcyclohexene derivatives were recorded as previously described.[1b]

6-Acetyl-1-methylcyclohexene.—The procedure used was adapted from that of Deno and Chafetz.[23] To a stirred mixture of 16.3 g. (0.13 mole) of zinc chloride and 70 ml. of acetic anhydride at 0° was added 10.0 g. (0.1 mole) of methylcyclohexene. Stirring was continued at room temperature for 0.5 hr., cooling once to maintain the temperature of the reaction mixture below 35°. Excess water was then added, and the mixture stirred until hydrolysis of the acetic anhydride was complete. The reaction products were extracted with ether. The extract was washed with dilute sodium bicarbonate and water, dried over anhydrous sodium sulfate, and the ether then evaporated under reduced pressure. Distillation of the residue gave 9.5 g. (69%) of 6-acetyl-1-methylcyclohexene, b.p. 76–77° (13 mm.), $n^{25}D$ 1.4701; infrared spectrum, 5.86 μ (s); reported b.p. 77–80° (12 mm.),[23] $n^{20}D$ 1.4740;[23] infrared spectrum,[24] 5.85 μ (s). Gas-liquid chromatography showed a single peak.

6-Bromo-1-methyl-2-nitrocyclohexene and 6-Bromo-1-methyl-6-nitrocyclohexene.—The method employed was similar to that described for the synthesis of 6-bromo-6-nitro-1-phenylcyclohexene.[16] To 3.41 g. (0.024 mole) of 1-methyl-6-nitrocyclohexene[22] in 40 ml. of methanol was added 1.35 g. (0.025 mole) of sodium methoxide. The solution was stirred for 5 min. and then cooled to 5°. N-Bromosuccinimide, 4.45 g. (0.025 mole), was then added, and the mixture was stirred at 5° for several minutes and then at room temperature until a clear solution resulted (*ca.* 15 min.). The

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[18] J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting," W. A. Benjamin, Inc., New York, N. Y., 1961, p. 71 ff. Should either $J_{AX} = J_{AY}$, $J_{XY} \gg (\delta_X - \delta_Y) + (J_{AX} - J_{AY})/2$, or $J_{AX}(J_{AY}) = 0$ in AXY systems, the A part of the spectrum is simplified to a triplet.

[19] E. J. Corey and R. A. Sneen, *J. Am. Chem. Soc.*, **77**, 2505 (1955).

[20] Triplet absorptions from AXY-type systems may arise for reasons other than the equality of J_{AX} and J_{AY}.[18] In any event, the separation between terminal lines of the triplet will represent the sum of J_{AX} and J_{AY},[18] and twice the apparent dihedral angle (time averaged) derived from the triplet will represent the sum of the actual dihedral angles.

[21] See ref. 10 and 12 in paper I.[1b] If $(\chi_L - \chi_T)$ equal to 5.5×10^{-30} cm.^{3}/molecule as given by A. A. Bothner-By and Naar-Colin, *Ann. N. Y. Acad. Sci.*, **70**, 833 (1958), is used, the calculated shielding by axial C-4 methyl comes to about 0.09 p.p.m.

[22] F. G. Bordwell and E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **82**, 3588 (1960).

[23] N. C. Deno and H. Chafetz, *ibid.*, **74**, 3940 (1952).

[24] R. B. Turner and D. M. Voitle, *ibid.*, **73**, 1403 (1951).

reaction solution was then poured into 150 ml. of ether–100 ml. of water. The ether was washed with water, dried over sodium sulfate and evaporated under reduced pressure. Distillation of the residue gave 3.6 g. (67%) of brominated 1-methyl-6-nitrocyclohexenes, b.p. 60–75° (0.2 mm.). Infrared analysis[22] showed that this material consisted of about 60% of 6-bromo-1-methyl-2-nitrocyclohexene (conjugated nitro absorption at 6.56 μ) and about 40% of 6-bromo-1-methyl-6-nitrocyclohexene (unconjugated nitro absorption at 6.40 μ). The mixture was redistilled for analysis and boiled at 65–71° (0.2 mm.). Infrared analysis of this material gave 59% of conjugated nitro derivative and 41% of unconjugated nitro derivative.

Anal.[25] Calcd. for $C_7H_{10}BrNO_2$: C, 38.20; H, 4.58; N, 6.37. Found: C, 37.97; H, 4.71; N, 6.53.

Acknowledgment.— The author wishes to express his gratitude to the National Science Foundation for a postdoctoral fellowship and to Professor M. M. Kreevoy for his constructive criticisms and comments.

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(25) The author wishes to thank Mrs. O. Hamerston for the analysis.

Reaction of Polyglycols with Phosphorus Pentafluoride

J. V. KARABINOS AND J. J. HAZDRA[1]

Olin Mathieson Chemical Corporation, New Haven, Connecticut

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Diethylene glycol and polyglycols, as well as their diethers, gave dioxane upon treatment with phosphorus pentafluoride. Under the same conditions, bis-1,4-hydroxyethylpiperazine was synthesized from diethanolamine and thiodiethylene glycol gave both 1,4-oxathiane and 1,4-dithiane.

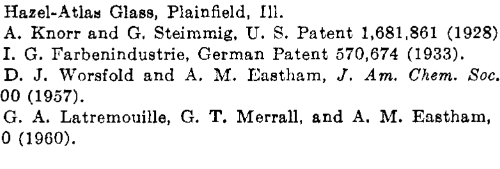
The early patent literature[2] reveals that ethylene and diethylene glycols as well as the monoethyl ether of diethylene glycol can be converted to dioxane by refluxing with catalytic amounts of concentrated sulfuric acid. Later work[3] describes similar results with polyethylene and polypropylene glycols. However, very few experimental data are given in either reference.

Eastham and his co-workers[4] have shown that in the cationic polymerization of ethylene oxide, for example with stannic chloride or boron trifluoride, some depolymerization of polyglycol occurs with concomitant formation of dioxane.

On the other hand it was observed[5] that triethyloxonium fluoroborate (Et_3OBF_4) caused almost complete depolymerization of polyethylene glycols to dioxane. It also has been reported[6] that ethylene and propylene oxides and even tetrahydrofuran can be polymerized by phosphorus pentafluoride to the corresponding polyglycols; however, there is no mention made of any depolymerization of the products.

This report describes the reaction of certain polyglycols and their derivatives with catalytic amounts of phosphorus pentafluoride to yield dioxane under relatively mild conditions.

The reaction can be represented as



Dioxane was formed in the above reaction from the glycols, their diethers, and diesters. However, under the same reaction conditions, the monoethers of ethylene and diethylene glycols did not produce dioxane and the starting materials were recovered in most part unchanged. An explanation of this anomaly is not obvious.

It should also be noted that the by-product of this reaction proved to be water from the glycols themselves and the corresponding ether from the glycol diethers; for example, dimethyl ether was isolated and identified from the dimethyl ether of diethylene glycol. In like manner the diacetate of diethylene glycol gave acetic anhydride as the by-product along with dioxane.

When diethanolamine was treated with phosphorus pentafluoride only trace amounts of morpholine were obtained. Instead, bis-1,4-dihydroxyethylpiperazine was isolated in 30% yield. Thiodiethylene glycol under the same conditions gave mainly 1,4-oxathiane along with lesser amounts of 1,4-dithiane.

Experimental

General Reaction Procedure of Phosphorus Pentafluoride with Substituted Glycols.—In a 500-ml. three-neck flask fitted with a condenser, sealed stirrer, and a Weston dial thermometer, 0.25 to 1.0 mole of glycol and, respectively, 0.025 to 0.1 mole *p*-chlorophenyldiazonium hexafluorophosphate were added. The use of less than 10 mole % of *p*-chlorophenyldiazonium hexafluorophosphate decreased the yield measurably, whereas an excess of 10 mole % did not increase the yield of the reaction. Since *p*-chlorophenyldiazonium hexafluorophosphate decomposed between 100–150° to yield pure phosphorus pentafluoride, the reaction mixture was heated to 120–150° and stirred for 24 hr. The mixture then was distilled twice from a Claisen head and

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(1) Hazel-Atlas Glass, Plainfield, Ill.

(2) A. Knorr and G. Steimmig, U. S. Patent 1,681,861 (1928).

(3) I. G. Farbenindustrie, German Patent 570,674 (1933).

(4) D. J. Worsfold and A. M. Eastham, *J. Am. Chem. Soc.*, **79**, 897, 900 (1957).

(5) G. A. Latremouille, G. T. Merrall, and A. M. Eastham, *ibid.*, **82**, 120 (1960).

(6) E. L. Muetterties, U. S. Patent 2,856,370 (1958).