Unexpected n-π^* Absorption of a Spiro Ketone from 2-Phenylcyclohexanone-2-acetic Acid

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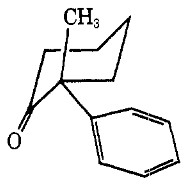
2-Phenylcyclohexanone-2-acetic acid, when treated with either sulfuric acid or polyphosphoric acid, rearranged with loss of water to form the lactone of 3-(1-hydroxy-1-cyclopentyl)cinnamic acid. The lactone was synthesized by ozonolysis of the glycol obtained by addition of allylmagnesium chloride to 1-benzoylcyclopentanol. The rearrangement of the keto acid was prevented by protection of the ketone group with ethanedithiol. The dithioketal was cyclized to the indanone, this was reduced to the indanol, and this was hydrolyzed to spiro(cyclohexan-2-one-1,1′-indan-3′-ol). In contrast to expectation, the n-π^* absorption of this ketone was substantial.

Cookson originally proposed[1] that exalted n-π^* transitions arose most significantly in α-phenyl ketones when the planes of the carbonyl group and the phenyl group faced each other. This idea has been supported in recent reports.[2,3] Reconciliation of the data for certain ketones remains difficult, however. For example, the spectrum of 2-phenylcyclohexanone (290 mμ, 17, EtOH)[4] is easily explicable (the planes are orthogonal and the phenyl group is equatorial) but that for 2-methyl-2-phenylcyclohexanone (294 mμ, 100, EtOH)[5] is not. True, a conformational equilibrium can be proposed,[5] but this seems quantitatively unsatisfactory. Conformation **9e**, surely the major one, would have no exaltation in the 290-mμ region, while **9a** would have an extinction coefficient of about 125.[6] An extinction coefficient of 50-60 would seem more appropriate for **9e**-**9a**. The validity of this argument, however, rests upon the correctness of the assumed value for **9e**. For this reason, spiro ketone **10**, which must be equivalent to **9e** for steric reasons, was desired.



9e

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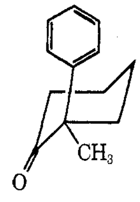
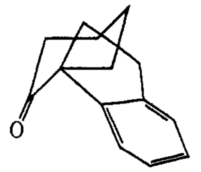


9a

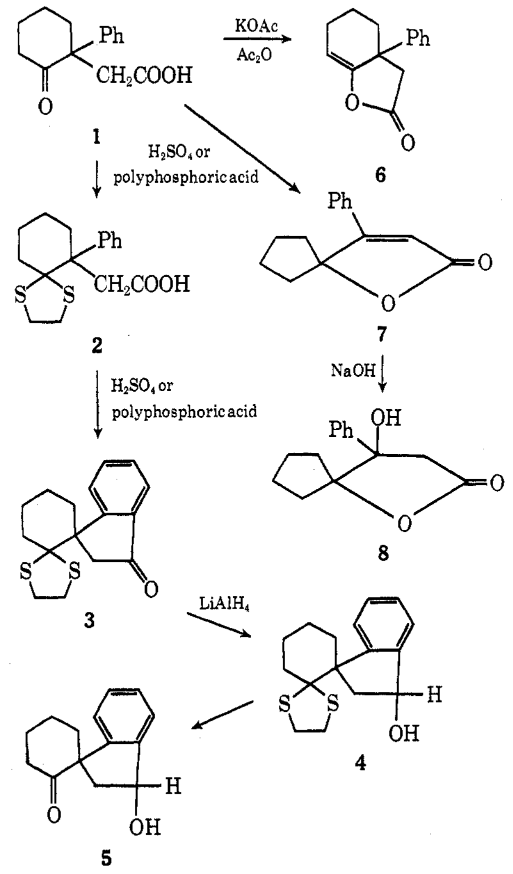


10

Results

The synthetic route to spiro ketone **5**, a hydroxylated variation of **10**, is shown in Scheme I. The starting compound, 2-phenylcyclohexanone-2-acetic acid (**1**), was prepared from 2-phenylcyclohexanone[7] by two different routes: (1) the formate blocking method of Ireland[8] and (2) direct alkylation of the ketone with sodamide and ethyl iodoacetate.[9] Treatment of keto acid **1** with polyphosphoric acid or sulfuric acid gave a lactone, **7**. The nmr spectral properties (5, s, δ 7.5; 1, s, 6.3; 8, m, 2.1) and the intense uv spectrum (275 mμ, ϵ 16,500, EtOH) suggested strongly the cinnamate structure. The lactone was resistant in the extreme to saponification.[10] Boiled with 20% sodium hydroxide, it gave a hydroxy derivative,[11] **8**. These properties strongly indicated structure **7**. This proposal is examined in detail in the third paragraph of this section. The ketone group in **1** therefore required protection prior to treatment with acids. With ethanedithiol,[12] **1** gave the dithioketal **2**, mp 162–164°. The ketone could not be made to react with the new reagent, 1,2-dimethyl-4,5-di(mercaptomethyl)benzene.[13] The di-

SCHEME I



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[1] R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956).

[2] S. MacKenzie, S. F. Marsocci, and H. C. Lampe, *J. Org. Chem.*, **30**, 3328 (1965).

[3] R. Gencarelli, H. Abajian, P. Irving, and S. MacKenzie, *ibid.*, **35**, 2673 (1970).

[4] W. C. Wildman and R. B. Wildman, *ibid.*, **17**, 581 (1952).

[5] P. Colard, I. Elphimoff-Felkin, and M. Verrier, *Bull. Soc. Chim. Fr.*, 516 (1961).

[6] The value chosen is based on the spectrum of 2,2-diphenylcyclohexanone: W. B. Bennet and A. Burger, *J. Amer. Chem. Soc.*, **75**, 84 (1953).

[7] M. S. Newman and M. D. Farbman, *ibid.*, **66**, 1550 (1944).

[8] R. A. Ireland and J. A. Marshall, *J. Org. Chem.*, **27**, 1615 (1962).

[9] D. Ginsburg and R. Pappo, *J. Chem. Soc.*, 1524 (1953).

[10] This is generally typical for α,β-unsaturated lactones of tertiary alcohols: F. Korte and D. Scharf, *Chem. Ber.*, **95**, 443 (1962); W. C. Bailey, *et al.*, *J. Org. Chem.*, **33**, 2819 (1968).

[11] Such a reaction was seen for triphenylcrotonolactone: Dutch Patent 6,412,872 (1965); *Chem. Abstr.*, **63**, p16429*f* (1965).

[12] L. F. Fieser, *J. Amer. Chem. Soc.*, **76**, 1945 (1954).

[13] I. Shahak and E. D. Bergmann, *J. Chem. Soc. C*, 1005 (1966).

thioketal gave, on treatment with sulfuric or polyphosphoric acid, the indanone **3**, mp 144–146°. Reduction of this with lithium aluminum hydride gave the indanol **4**. Chromatography on silica gave the two isomers, mp 80–83° (10 parts) and 162–164° (1 part). The major isomer, when treated with $HgCl_2$ and $CdCO_3$,[14] gave the spiro ketone **5**. This liquid had an nmr spectrum which suggested that it was a mixture of stereoisomers arising by racemization at the benzyl alcohol site. The ketone had an exalted uv spectrum (290 mμ, ε 183, EtOH).

An explanation for this exaltation must be sought. Provisionally advanced is the suggestion that the cyclohexane ring of this ketone has adopted a twist or a flattened chair conformation. Little support is found in the literature for this idea. The best known cases of nonchair conformations involve 1,3-diaxial alkyl interactions.[15] These are present in 3,3,5-trimethyl-5-phenylcyclohexanones.[16] The simpler 2-methyl-2-phenylcyclohexanones appear not to have been studied in this regard. Table I gives the results of an inspection of Dreiding models of spiro[2,2-indanocyclohexanone] (**10**). Of the six boat forms listed in Table I, three have very serious repulsion between the hydrogen atom of the phenyl ring and the hydrogens of the cyclohexane ring. The other three boat forms have less serious repulsion between the indan methylene group and the hydrogens of the cylcohexane ring as a main factor. The cyclic path of rotatory change connecting these boat forms has two transition points which represent a change of the principal factor of repulsion. At these two transition points, twist boat forms can be found which have lower repulsion energies. Of course, the boat forms also have two sets of eclipsed hydrogen atoms at a distance of about 2.25 Å but this energy is no longer the major factor. Table I admits the possibility, then, that twist–boat forms may contribute to the conformational population of **10**. One of the full-boat forms (prow 3) may also contribute.

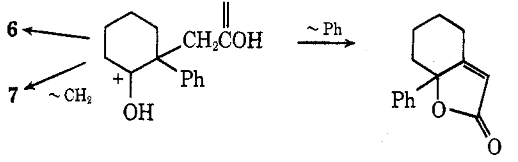
TABLE I

TABULATION OF SHORTER H–H REPULSION DISTANCES FOR SPIRO[INDANOCYCLOHEXANONE]

Prow[a]	Eclipsed H[b]	Methylene[c]	Phenyl[c]	*d*
2	3, 4	1.6, 1.6	2.25	0°
3	4, 5	2.0, 3.0	2.25, 2.5	60°
e		2.25, 2.5	2.0, 2.25	90°
4	5, 6	2.0	1.5, 2.0	120°
5	3, 4	2.5, 2.5	Short	120°
6	4, 5	2.5, 2.5	1.5, 1.75	60°
e		2.0, 2.25	2.25	20–30°
1	5, 6	2.0, 2.0	2.5, 2.6	0°
f		2.0, 2.0	2.25	0°

[a] Given is the number of the carbon atom in the cyclohexane ring which is the prow of the boat form. [b] For additional identification, given is the location of the cyclohexane carbon atoms which have eclipsed hydrogen atoms. [c] Several of the shorter H–H repulsion distances, measured in Dreiding models, are given for the methylene group and for the phenyl group of the indano system. [d] The angle made by the carbonyl group with the plane containing carbons 1 and 2 and the carbon of phenyl attached to the cyclohexane ring. [e] Twist–boat forms placed in the table where a different repulsion phenomenon becomes more important. [f] For comparison of repulsion distances, given are data for the chair conformation with the phenyl group equatorial.

Various workers have studied the rearrangement of ketones. It was originally noted[17] that only tetra- or trisubstituted cycloalkanones rearranged in acid, but subsequently many exceptions have been observed. Ketones having lesser degrees of substitution can rearrange when additional factors favorable to such reaction exist. Such factors can be increased resonance energy,[18] relief of steric strain,[18] relief of small-ring strain,[19] and, most appropriate to the present study, the formation of lactone rings. 2-Methylcycloheptanone-2-acetic acid with incidental substituents rearranged[20] to a spiro[5.6]lactone. The present circumstance is different in the fact that the ring contraction is 6 to 5, not 7 to 6, and that a phenyl group, normally prone to migrate easily, is also present. Several possible acid-catalyzed events should be considered.



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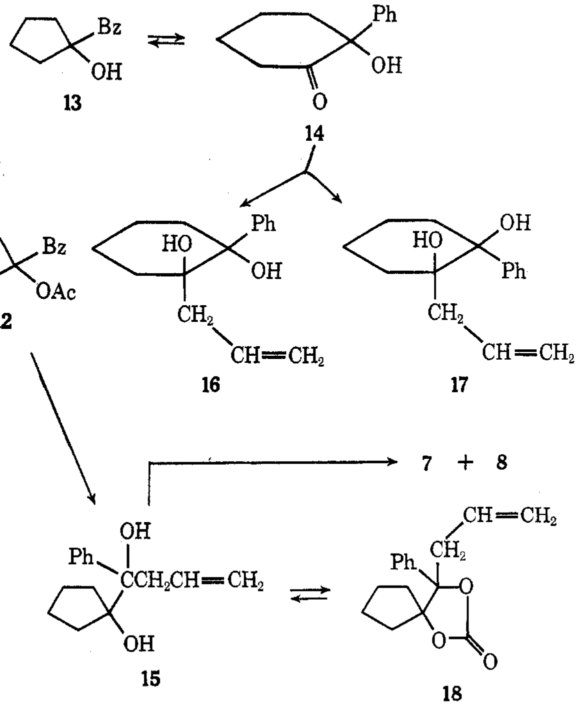
Although neither the enol lactone **6** nor lactone **11** would be expected to have the spectral properties of the rearrangement product, it was advisable to seek an independent structure proof for **7**. The synthetic work is outlined in Scheme II.

SCHEME II



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[14] J. English, Jr., and P. H. Griswold, *J. Amer. Chem. Soc.*, **67**, 2040 (1945).

[15] N. L. Allinger and M. A. Rogers, *ibid.*, **84**, 4561 (1962).

[16] M. Balasubramanian and A. D'Souza, *Tetrahedron*, **25**, 2973 (1969).

[17] S. Barton and C. R. Porter, *J. Chem. Soc.*, 2483 (1956).

[18] H. D. Zook, W. E. Smith, and J. L. Greene, *J. Amer. Chem. Soc.*, **79**, 4436 (1957).

[19] R. L. Cargill, D. M. Pond, and S. D. LeGrand, *J. Org. Chem.*, **35**, 359 (1970).

[20] B. W. Roberts, S. C. Welch, and J. L. Steed, *J. Chem. Soc. D*, 535 (1969).

The obvious synthesis (**12** + NaH) failed, as did additions of various ester anions to **12** or **13**. Isolated in such instances was the mixture of **13** and **14**. Allylmagnesium chloride reacted with **13** to give a liquid glycol, **15**. Reaction with **14** (containing some **13**) gave three glycols,[21] easily separated by chromatography. Table II suggested, in analogy to the work of Price,[22] that the glycol of mp 57–60° is **17** (cis) and that of mp 80–82° is **16** (trans). The liquid glycol, which gave cyclopentanone when treated with lead tetraacetate, must be **15**.

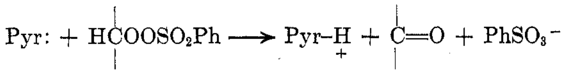
TABLE II

PER CENT REACTION OF GLYCOLS WITH PERIODATE, 2 MIN,[a] 25°

Glycol	pH[b] 7	8.5	11.5	11.9[c]	12
17			84	85	88
15				67	
16	68	79	50		13
Propylene	70	33			
Ethylene	14	4			
Pinacol	4	9			

[a] Reactions were not quenched; they stopped due to pH change. [b] The pH is that of the aqueous 0.02 *M* periodate which was added to the glycol in 50% diglyme. [c] Glycol was dissolved in 100% diglyme.

The liquid glycol **15** was also prepared from the solid 1-acetoxy-1-benzoylcyclopentane, prepared from benzoylcyclopentane and lead tetraacetate, and also by regeneration from the solid cyclic carbonate, **18**. Ozonolysis of **15**, followed by decomposition, distillation, and chromatography, gave lactone **7**. All three specimens of glycol **15** had the same ir spectrum and gave identical results on ozonolysis. The crystalline character of lactone **7** facilitated final purification. Since the initial six ozonolyses (two with each of the three glycol preparations) gave such disappointing yields (9–11% in each case) of **7**, an alternative to the thermal decomposition of the ozonide was sought. Under the assumption that the products of ozonolysis contained cyclic hydroperoxide,[23] decomposition by polar means was explored. Addition of benzenesulfonyl chloride caused a pyridine solution of the peroxidic material to boil. The yield of lactones was 47% (45% of **8** and 2% of **7**). The mechanism shown below is plausible.



$$\text{Pyr:} + \text{H}\overset{|}{\underset{|}{\text{C}}}\text{OOSO}_2\text{Ph} \longrightarrow \text{Pyr–}\underset{+}{\text{H}} + \overset{|}{\underset{|}{\text{C}}}\text{=O} + \text{PhSO}_3{}^-$$

Experimental Section

2-Phenylcyclohexanone-2-acetic Acid (from Ethyl Iodoacetate).—To a suspension of sodamide (from 10.7 g of sodium) in ether was added a solution of 83 g (0.475 mol) of 2-phenylcyclohexanone[7] in 100 ml of ether and 200 ml of benzene over a period of 2 hr. The mixture was refluxed for 10 hr, cooled, and treated with a solution of 100 g (0.47 mol) of ethyl iodoacetate in 100 ml of ether over a period of 1.5 hr. The mixture was refluxed for 4 hr and hydrolyzed with cold water. After extraction, the combined organic layers were washed four times with solutions of sodium thiosulfate and dried, and the solvents were removed by evaporation. The oil residue was refluxed for 4 hr with 500 ml of 10% NaOH, cooled, and extracted with ether. Evaporation gave 17 g of recovered ketone. Acidification of the aqueous layer gave 39.8 g (47%) of keto acid **1**: mp 134–136° (lit.[9] mp 133–134°); uv max (95% EtOH) 251 mμ (ε 202), 257 (260), 263 (203), 290 (97); nmr (CCl_4) δ 2.9 (d, 2, J = 2 Hz, CH_2COOH).

2-Phenylcyclohexanone-2-acetic Acid (from Blocked Ketone).—A solution of 57 g (1.46 mol) of potassium in 1.4 l. of dry *tert*-butyl alcohol was stirred under nitrogen. After addition of 88 g (0.364 mol) of 2-*n*-butylthiomethylene-6-phenylcyclohexanone,[8] the mixture was stirred at room temperature for 5 min. It was cooled in an ice bath and 357 g (2.33 mol) of methyl bromoacetate was added all at once. After the initial reaction had subsided, the mixture was refluxed for 2 hr. The excess *tert*-butyl alcohol was removed by distillation and 500 ml of water was added to the residue. After extraction with ether and solvent removal, the oily residue was treated with 500 ml of ethylene glycol and 500 ml of 25% KOH and refluxed for 15 hr. Cooling and extraction with ether gave 14 g of 2-phenylcyclohexanone. The aqueous layer was acidified to precipitate 38 g (67%) of **1**.

The Enol Lactone (6) of 2-Phenylcyclohexanone-2-acetic Acid.—One gram of 2-phenylcyclohexanone-2-acetic acid was mixed with 3 ml of acetic anhydride and 0.1 g of KOAc and refluxed for 4 hr. After standing overnight, the liquid was poured into water, extracted with ether, and washed liberally with portions of sodium bicarbonate solution. Distillation in a small glass tube gave colorless liquid: $n^{25}D$ 1.5630; uv max (C_6H_{12}) 205 mμ (ε 13,700), 252 (217), 258 (236), 261 (211), 263 (186), 268 (155); nmr (CCl_4) δ 5.4 (t, 1, vinyl H), 2.7 (s, 2, CH_2COO–).

Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found:[24] C, 78.29; H, 6.52.

3-(1′-Hydroxycyclopentyl)-3-phenylpropenoic Acid Lactone (7).—A solution of 11.5 g (0.049 mol) of 2-phenylcyclohexanone-2-acetic acid in 130 g of polyphosphoric acid was heated in an oil bath maintained at 84–92° for 3 hr. The solution became brown. After addition of water, extraction, and washing of organic layers, evaporation gave 10 g of neutral material. After four recrystallizations from ethanol–water, the yield of solid was 6.4 g (61%). Use of 90% sulfuric acid in place of polyphosphoric acid gave about the same yield of colorless solid: mp 74–76°; nmr (CCl_4) δ 7.5 (s, 5, Ph), 6.3 (s, 1, vinyl), 2.0–2.2 (m, 8, cyclopentane); uv max (95% EtOH) 275 mμ (ε 16,500).

Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.66; H, 6.74.

In a kinetic experiment, 0.5346 g (0.0025 mol) of the lactone was mixed with 200 ml of 0.106 *N* NaOH and the mixture was diluted to 500 ml with methanol. After 20 days at 20°, the titer was unchanged.

3-(1′-Hydroxycyclopentyl)-3-hydroxy-3-phenylpropanoic Acid Lactone (8).—A mixture of 3 g of the unsaturated lactone **7** and 50 ml of 20% NaOH was made homogeneous with ethanol and then refluxed for 5 days. Cooling gave 1 g of recovered **7**. Acidification and further cooling caused precipitation of 1.9 g of crude material, mp 102–124°. After five recrystallizations from ethanol–water, there was obtained 1.4 g (43%) of colorless solid: mp 123–124°; nmr (CCl_4) δ 7.45 (m, 5, Ph), 3.08 (q, 2, J = 17 Hz, CH_2COO), 3.2 (s, 1, OH), 1.3–2.3 (m, 8, cyclopentane). The uv spectrum was benzenoid.

Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94; O, 20.66. Found: C, 72.16; H, 7.04; O, 20.77.

Ethylene Dithioketal of 2-Phenylcyclohexanone-2-acetic Acid (2).—To a mixture of 10 g (0.043 mol) of the acid **1** and 20 ml of ethanedithiol was added with stirring 4 ml of boron trifluoride etherate. Within 5 min, the acid had dissolved and the solution became yellow. After stirring for another 5 min, the solution became cloudy. Stirring was continued at room temperature for 2 hr. Methanol was added to produce a clear solution which was then added to 400 ml of 10% NaOH. After filtration, acidification gave 10.5 g (80%) of crystals: mp 162–164°; nmr (CCl_4) δ 11.0 (s, 1, COOH), 7.6–7.2 (m, 5, Ph), 3.3 (d, 2, J = 7 Hz, CH_2COO), 3.0–1.4 (m, 12, ring H atoms). The uv spectrum was benzenoid.

Anal. Calcd for $C_{16}H_{20}O_2S_2$: C, 62.31; H, 6.52; S, 20.79. Found: C, 62.40; H, 6.33; S, 21.1.

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[21] The reaction of 2-hydroxy-2-phenylcyclohexane with phenyllithium gave only *trans*-diphenylcyclohexanediol: P. Tomboulian, *J. Org. Chem.*, **26**, 2652 (1961).

[22] C. C. Price and M. Knell, *J. Amer. Chem. Soc.*, **64**, 552 (1942), showed that *cis*-cyclohexanediol reacted 60 times faster than the trans isomer at pH 10.

[23] A. Rieche, M. Schulz, and D. Becker, *Chem. Ber.*, **98** (11), 3627 (1965).

[24] All analyses were performed by Micro-Analysis, Inc., Wilmington, Del. 19808.

Dispiro[1,3-dithiolane-2,1′-cyclohexane-2′,1″-indan-3″-one] (3).—To 6.5 g (0.021 mol) of finely powdered ketal **2** was added with mechanical stirring 140 g of warm (50–60°) polyphosphoric acid. With continued stirring, the contents were heated over 1 hr to 73–78° and maintained at this temperature for 5.5 hr. The oil bath was then removed and the stirring was continued for an additional 1 hr. The contents were cooled by an ice bath and ice water was added. The contents became warm and the odor of sulfur compounds was apparent. The solid which precipitated was dissolved in ether and the aqueous layer was extracted with ether. The combined ether portions were extracted with 100 ml of 10% NaOH and four times further with 50-ml portions. Acidification of the aqueous layer gave 0.6 g (0.002 mol) of recovered keto acid **1**. The ether was evaporated to give solid which was recrystallized from ethanol. Obtained was 2.85 g (52.5%) of colorless solid: mp 144–146°; uv max (95% EtOH) 242 $m\mu$ (ϵ 11,286), 285 (2943); nmr (CCl_4) δ 8.2–7.5 (m, 4, aromatic), 3.05–2.0 (m, 14, aliphatic).

Anal. Calcd for $C_{16}H_{18}OS_2$: C, 66.16; H, 6.25; S, 22.08. Found: C, 66.27; H, 6.15; S, 22.10.

Dispiro[1,3-dithiolane-2,1′-cyclohexane-2′,1″-indan-3″-ol] (4).—To a stirred suspension of 0.73 g (0.019 mol) of lithium aluminum hydride in 50 ml of anhydrous ether was added a solution of 3.16 g (0.011 mol) of **3** in ether over a period of 30 min. The mixture was refluxed overnight, cooled, and hydrolyzed with saturated ammonium chloride solution. Evaporation of the ether gave a solid which was added to a column made up in a 1-in. tube with 100 g of silica and benzene. Elution with benzene gave ten parts of the more abundant isomers: mp 80–83°; nmr ($CDCl_3$) δ 7.75 (m, 1, aromatic), 7.25 (m, 3, aromatic), 4.95 (q, 1, J = 4 Hz, CHOH), 3.72 (s, 1, OH), 3.3–1.2 (m, 14, aliphatic); uv max (95% EtOH) 251 $m\mu$ (ϵ 459), 258 (489), 265 (543), 272 (453).

Anal. Calcd for $C_{16}H_{20}OS_2$: C, 65.71; H, 6.89; S, 21.93. Found: C, 65.77; H, 6.94; S, 21.89.

Continued elution gave one part of the less abundant isomer: mp 162–164°; nmr (CCl_4) δ 7.8 (m, 1, aromatic), 7.4 (m, 3, aromatic), 5.7 (t, 1, J = 7 Hz, CHOH), 3.4–1.5 (m, 15, aliphatic + OH); uv max (95% EtOH) 252 $m\mu$ (ϵ 450), 257 (527), 263 (615), 272 (534).

Anal. Calcd for $C_{16}H_{20}OS_2$: C, 65.71; H, 6.89; S, 21.93. Found: C, 65.75; H, 6.83; S, 21.94.

Spiro[cyclohexan-2-one-1,1′-indan-3′-ol] (5).—To a solution of 0.6 g of dispiro compound **4**, mp 80–83°, in 60 ml of acetone and 3 ml of water were added 1.3 g of cadmium carbonate and 1.3 g of mercuric chloride. The reaction mixture was stirred for 6 days and 0.2 g of each of the inorganic salts was added four times during that period. The solid was filtered off, the acetone was removed by distillation, and the solid was extracted with ether. Ether-insoluble material was discarded. The ether solution was washed three times with 100-ml portions of 10% KI, once with water, and once with saturated NaCl solution. The oil which remained after removal of the ether was placed in a Kragen tube under high vacuum and distilled. A small amount of material which distilled below a bath temperature of 160° was discarded. Obtained was a highly viscous oil: nmr ($CDCl_3$) δ 7.4 (m, 4, aromatic), 5.15 (m, 1, CHOH), 3.0–1.8 (m, 11, aliphatic + OH); uv max (95% EtOH) 257 $m\mu$ (ϵ 548), 263 (693), 268 (646), 290 (183).

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46; O, 14.8. Found: C, 77.58; H, 7.18; O, 14.86.

The ketone formed a 2,4-dinitrophenylhydrazone, mp 153–155°.

Anal. Calcd for $C_{20}H_{20}N_4O_5$: C, 60.6; H, 5.09; N, 14.13. Found: C, 60.46; H, 4.90; N, 14.09.

Benzoylcyclopentane (19).—To the cyclopentylmagnesium bromide prepared from 89.3 g (0.6 mol) of bromocyclopentane, 14.58 g (0.6 g-atom) of magnesium, and 2 l. of ether, was added slowly with mechanical stirring 41.2 g (0.4 mol) of benzonitrile. Solid precipitated. After standing overnight, the mixture was poured into water and acidified with 100 ml of concentrated HCl. The water layer was separated, heated to 90°, recooled, and extracted with ether. The combined ether portions gave, on distillation, a yield of 50 g (72%) of ketone[25] **19**.

1-Acetoxy-1-benzoylcyclopentane (12).—Following the procedure of Henbest,[26] 53.8 g (0.1336 mol) of lead tetraacetate was dissolved in 2 l. of anhydrous benzene. There was added all at once with mechanical stirring 21 g (0.1215 mol) of **19**. This was followed by 50 g of boron trifluoride etherate. The solution, originally orange, became yellow. It was heated slowly to 65° and then allowed to stand for 2 weeks. Cold water (500 ml) was added and the organic layer was separated and dried. Distillation gave 35% of recovered **19** and 45% of liquid boiling at 140–144° (1 mm) which soon solidified. Obtained from cyclohexane were colorless crystals: mp 49–50°; nmr (CCl_4) δ 7.8–7.3 (m, 5, aromatic), 1.75 (s, 3, OAc), 2.6–1.2 (m, 8, aliphatic).

Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.95. Found: C, 72.43; H, 6.84.

1-(1′-Hydroxycyclopentyl)-1-phenyl-3-butenol-1 (15).—To the Grignard reagent prepared from 15.5 g (0.2 mol) of allyl chloride, 9.7 g (0.4 g-atom) of magnesium, and 350 ml of anhydrous ether was added a solution of 5.7 g (0.025 mol) of 1-acetoxy-1-benzoylcyclopentane. The mixture was allowed to stand overnight. The mixture was then poured into 1 l. of ice–water slush. After the ice melted, the mixture was poured into a separatory funnel and the layers were allowed to separate over an hour or two. Neither acid nor ammonium chloride was added. The thick water layer was extracted twice with ether, considerable time again being allowed for layer separation. After removal of the ether, the oil was subjected to chromatography on silica. Only one fraction was obtained. Repeated efforts to cause the oil to solidify were unsuccessful. Obtained was 3.1 g (55%) of viscous oil, bp 145–148° (1 mm), $n^{20}D$ 1.5446.

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.54; H, 8.68.

One gram of the glycol was treated with 2.0 g of lead tetraacetate and 20 ml of acetic acid. The mixture was allowed to stand overnight. Steam distillation was conducted until 60 ml of distillate was collected. Addition of 2,4-dinitrophenylhydrazine reagent gave an orange precipitate which was impure. After three recrystallizations from ethanol, the derivative, mp 141–143°, was bright yellow. The yield at this point was 9%. A mixture melting point with the derivative prepared from cyclopentanone was not depressed.

Cyclic Carbonate 18.—Into an ice-cold solution of 25 g (0.107 mol) of glycol **15**, 32 g of pyridine, and 125 ml of chloroform was bubbled 19.8 g (0.20 mol) of phosgene. The solution was kept in ice for 5 hr and then allowed to warm up to room temperature overnight. It was poured into much ice (brisk reaction) and the chloroform layer separated. It was washed with water and twice with portions of sodium bicarbonate solution. The chloroform was evaporated and the liquid residue, previously found to smoke badly on attempted distillation, was added to a 1 × 24 in. column of silica made up with benzene. Elution with benzene (1500 ml) gave 21.6 g, bp 176–180° (1 mm). It solidified on cooling and was recrystallized from 25 ml of cyclohexane and then from 25 ml of ethanol. Obtained was 15.9 g (57%) of large blocks: mp 80–82°; nmr (CCl_4) δ 7.4 (s, 5, Ph), 5.0 (m, 3, vinyl), 2.9 (d, 2, J = 5 Hz, allylic), 2.4–1.3 (m, 8, cyclopentane); ir (Nujol) 1790 cm^{-1} (ester), no OH band.

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.38; H, 7.00.

To a solution of 2.58 g (0.01 mol) of cyclic carbonate **18** in 10 ml of dry tetrahydrofuran was added 0.38 g (0.01 mol) of lithium aluminum hydride. After 2 hr of stirring at room temperature, the liquid was treated with a few milliliters of ethanol and poured into cold water. Extraction with ether gave a liquid which was distilled in a small apparatus. The ir spectrum of this preparation was identical with that of the glycol prepared from 1-acetoxy-1-benzoylcyclopentane.

1-Benzoylcyclopentanol (13) and 2-Hydroxy-2-phenylcyclohexanone (14).—Compound **13** was made by the addition of the tetrahydropyranyl ether of cyclopentanone cyanohydrin to phenylmagnesium bromide.[5,27] The hydroxy ketone gave, on retreatment with dihydropyran, the tetrahydropyranyl ether, bp 127–130° (1 mm), $n^{25}D$ 1.5335.

Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.45; H, 7.95.

There was no advantage, however, to using this ether in place of **13** itself in the preparation of glycol **15**. Benzoylcyclo-

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[25] Due to the tendency of cyclopentylmagnesium bromide to reduce carbonyl compounds, the ketone has usually been made by the Friedel–Crafts synthesis: D. H. Hey and O. C. Musgrave, *J. Chem. Soc.*, 3156 (1949).

[26] H. B. Henbest, D. N. Jones, and G. P. Slater, *ibid.*, 4472 (1961).

[27] I. Elphimoff-Felkin, *Bull. Soc. Chim. Fr.*, 784 (1955).

pentanol was isomerized to a mixture which was largely **14** by powdered KOH.[5]

cis- **and** *trans*-**1-Allyl-2-phenyl-1,2-cyclohexanediol.**—Into the Grignard reagent prepared from 30.6 g (0.40 mol) of allyl chloride, 12.1 g (0.50 g-atom) of magnesium, and 700 ml of anhydrous ether was added a solution of 8.7 g (0.05 mol) of ketone, largely 2-hydroxy-2-phenylcyclohexanone, in 125 ml of ether. The reaction was vigorous and a thick paste formed. After standing overnight, the mixture was poured into ice water. No acid or ammonium chloride was added. After layer separation, the thick aqueous layer was extracted twice with ether. The ether portions were combined and distilled. Vacuum distillation gave 7.5 g of highly viscous oil. A portion (2.25 g) was placed on a column of silica,[28] 1 × 25 in., made up with benzene. Elution was with benzene, and 250-ml portions were collected. The residues of bottles 4–8, after several cycles of cooling and rewarming, finally solidified. Large lumps (0.7 g, mp 57–60°) were obtained from cyclohexane.

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.83; H, 8.82.

The residues from bottles 9–16 remained liquid. When the flow of 5% ethyl acetate in benzene was started, a second series of bottles (17–21) gave residues which solidified still more slowly than those of bottles 4–8. Seeding was most advantageous. Fractions 17–21, when dissolved in hot cyclohexane, gave fine hairs, mp 82–83°.

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.74; H, 8.78.

A larger run (5.8 g) on the same size column gave 2.1 and 1.7 g.

Ozonolysis of Glycol 15.—The glycol, prepared from 2.58 g of cyclic carbonate as described above, was dissolved in 100 ml of ethyl acetate, cooled to −70° in a bath of ethyl acetate and Dry Ice, and treated with oxygen containing 1% ozone until the solution developed a faint blue color. Evaporation of the ethyl acetate under reduced pressure (20 mm) without heating gave a colorless, thick oil. It could be stored at room temperature for several days but gradually became tan, then darker brown. Its ir spectrum showed that hydroxyl, carbonyl, and perhaps lactone groups were present. When, in an earlier run, the liquid was heated, it decomposed abruptly but without detonation. The presence of zinc dust made no difference in this property. The mixture became black. A portion (1.18 g) of the thick oil was, directly after preparation, dissolved in 10 ml of pyridine. Faint heat evolution was noted. When 2 ml of benzenesulfonyl chloride was added with stirring, the pyridine came to a boil rapidly. It was allowed to cool to room temperature and then allowed to stand overnight. A small amount of precipitate formed. The mixture was poured into water and extracted with ether. Evaporation of the ether and traces of residual pyridine gave an extremely viscous liquid, no longer sensitive to heat. Addition of 1 ml of cyclohexane and 1 ml of benzene permitted direct crystallization of 0.384 g (32.5%) of hydroxylactone **8**. Chromatography on silica of the residue from the crystallization gave 2% of unsaturated lactone **7** and an additional 12.7% of **8**. The total yield was thus 47%. The lactones so prepared did not depress the melting points of the lactones produced by rearrangement.

Registry No.—**1,** 3645-89-4; **2,** 34219-59-5; **3,** 34201-78-0; **4,** 34201-79-1; **5,** 34201-80-4; **5** 2,4-DNP, 34219-60-8; **6,** 34219-61-9; **7,** 34219-62-0; **8,** 34201-81-5; **12,** 34219-63-1; **14** tetrahydropyranyl ether, 34219-64-2; **15,** 34219-65-3; **16,** 34216-97-2; **17,** 34216-98-3; **18,** 34201-82-6.

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[28] Size was 70–325 mesh. EM Laboratories, Inc., Elmford, N. Y. 10523.

Structural and Conformational Studies of 2-Phenyl-1,3,2-diaza- and -dioxaboracycloalkanes

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A series of 1,3,2-diaza- and -dioxaboracyclohexanes have been investigated by means of proton and boron nmr in order to obtain information concerning the conformation of the rings, hybridization and stereochemistry of the nitrogens, and effects of ring substitution on boron chemical shifts. The data suggest that the N–C_4–C_5–C_6–N and the O–C_4–C_5–C_6–O regions adopt normal rapidly inverting chair type conformations. Substituents on nitrogen appear to strongly prefer equatorial orientations presumably because of extensive nitrogen to boron π bonding. The difference in boron chemical shifts observed for five- and six-membered rings in the diazaboracycloalkanes may be explained by assuming pyramidal hybridization of the nitrogens.

During the past five years considerable interest has been directed toward structural and conformational studies of various six-membered ring heterocycle containing more than one heteroatom including dioxa-,[2,3] dithia-,[2,4] and diazacyclohexanes.[2a,5] In contrast, relatively little conformational and structural information is available concerning boron-containing heterocycles. Of particular interest in this area are boron heterocycles containing additional adjacent heteroatoms such as nitrogen or oxygen which have lone electron pairs and thus are capable of π overlap with the vacant p orbital on boron, a topic of considerable interest.[6] In line with our general interest in conformational analysis of heterocyclic compounds[4,5a] and in bonding between boron and other heteroatoms,[6] we have undertaken a proton and ^{11}B nmr spectral study of a series of 2-phenyl-1,3,2-diazabora- and -dioxaboracyclohexanes with the aim of obtaining information concerning the shape of the rings, the stereochemistry about the nitrogens in the diaza derivatives, and the bonding between boron and other heteroatoms.

A considerable amount of evidence has been accumulated which indicates that substantial π bonding occurs between boron and adjacent atoms which bear lone electron pairs.[6,7] In cases where the adjacent atom is

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[2] Excellent reviews concerning conformational analysis of heterocyclic compounds containing more than one heteroatom are available. See (a) E. L. Eliel, *Accounts Chem. Res.*, **3**, 1 (1970), and references cited therein; (b) C. Romers, C. Altona, H. R. Buys, and E. Havinga, "Topics in Stereochemistry," Vol. 4, Wiley, New York, N. Y., 1969, and references cited therein; (c) C. H. Bushweller, "Mechanisms of Reactions of Sulfur Compounds," Vol. 5, Intra-Science Research Foundation, Santa Monica, Calif., 1969, p 75, and references cited therein.

[3] F. W. Nader and E. L. Eliel, *J. Amer. Chem. Soc.*, **92**, 3050 (1970).

[4] E. L. Eliel and R. O. Hutchins, *ibid.*, **91**, 2703 (1969).

[5] (a) R. O. Hutchins, L. D. Kopp, and E. L. Eliel, *ibid.*, **90**, 7174 (1968); (b) P. J. Halls, R. A. Y. Jones, A. R. Katritzky, M. Snarey, and D. L. Trepanier, *J. Chem. Soc. B*, 1320 (1971); (c) H. Booth and R. M. Lemieux, *Can. J. Chem.*, **49**, 779 (1971).

[6] For a review of the pertinent literature see F. A. Davis, I. J. Turchi, and D. N. Greeley, *J. Org. Chem.*, **36**, 1300 (1971).

[7] K. Niedenzu and J. W. Dawson in "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, p 392.