proved to be identical with cyclohexyloxindole from the catalytic reduction (part A) by mixture melting point and infrared spectral comparison.

Reduction of Isoindigo.—A hot suspension of isoindigo (0.5 g.) in 2-propanol (40 ml.) and water (5 ml.) was treated with sodium borohydride (0.12 g.). Within 10 min. all of the solid had dissolved, and the boiling solution was colorless. More water (20 ml.) was added, and the mixture was kept hot 20 min. longer. The solution was concentrated under reduced pressure to one-third of the original volume, and a solid began to separate. The suspension was reheated and the solid was dissolved by addition of alcohol. On standing, the hot filtered solution deposited colorless crystals, 0.5 g., m.p. 258°. Recrystallization from alcohol raised the melting point to 272–274°. Mixture melting point and infrared spectra showed the product was identical with a sample of leucoisoindigo prepared by zinc–acetic acid reduction of isoindigo.[13]

Long-Range Deshielding by Chlorine

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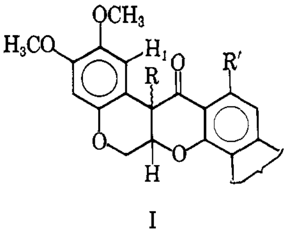
Long-range shielding and deshielding effects have been known to n.m.r. spectroscopists for some time.[2] Most of the clearly defined examples involve the anisotropy of unsaturated functions. We report herein the observation of an unusually large chemical shift produced by a chlorine atom five bonds distant from the shifted proton.

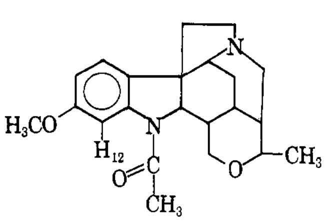
Compounds **2–5**, Table I, having R_3 = Cl, all show an absorption in the range τ 0.97–1.20, integrated intensity of one proton. This peak has been assigned to H_4 on the aromatic ring. It appears as the X portion of an ABX system: an intense quartet and two weak combination bands.[3,4] The AB portion of the spectrum, H_2 and H_3, is complicated by overlap and/or coupling to H_1, so that the values for J_{AX} and J_{BX} cannot be obtained. However, the sum $|J_{AX} + J_{BX}| = 10.0$ c.p.s. can be measured.

Upon reductive removal of the chlorine atom (compound **1**) the H_4 peak merges with the $H_2 + H_3$ resonance at *ca.* τ 2.0.

A long-range deshielding effect, produced by the anisotropy of the carbon–oxygen double bond, previously has been noted for the carbonyl group in formally similar structures. For example, Crombie and Lown[5] have used the shielding of the 1-hydrogen by the 12-carbonyl to assign the geometry of the B/C ring fusion in a series of rotenoids (I). Anet[6] has found that restricted rotation of the N-acetyl group in strychnospermine (II) produces a downfield shift of the aromatic proton at C-12. At room temperature, rotation of the acetyl group is sufficiently rapid that the two possible environments for C-12 are averaged out. At lower temperatures, that conformation having the carbonyl adjacent in space to C-12 displays the unusual shift. The geometry of this frozen conformation closely resembles that of compounds **1–5**.



I

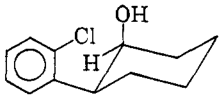


II

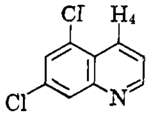
A few reports of such deshielding by chlorine are scattered through the literature. Huitric[7] recently has suggested that, in *cis*-2-(*o*-chlorophenyl)cyclohexanols (III), the *o*-chlorine causes a downfield shift of the 1-hydrogen resonance. However, the shift is smaller by an order of magnitude than that observed in this work (0.1 p.p.m. *vs.* 0.8–1.0 p.p.m.).

The spectrum of 5,7-dichloroquinoline[8] (IV) shows a downfield shift of 0.48 p.p.m. for H_4 when compared to 5,7-dimethylquinoline. In this instance, the chlorine and the shifted proton are *four* bonds apart in a *conjugated* system; a part of the effect may be transmitted through the π-system. Similarly, the indicated aromatic protons of V[9] show a downfield shift of 0.52 p.p.m. when compared to the aromatic protons of 9,10-dihydroanthracene.

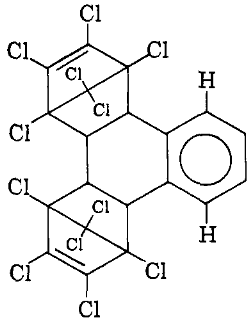
Finally, Osawa and Neeman[10] report chemical shifts for H_4 in the estrones (VIa and b) of τ 2.82 and 3.14, respectively, a difference of 0.32 p.p.m.



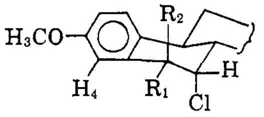
III



IV



V



VIa, R_1 = Cl; R_2 = H
b, R_1 = H; R_2 = Cl

It is possible that the great magnitude of the shift observed in our pyrrolo[1,2-*a*]quinoxalines results from both electrostatic electron withdrawal (a field effect) *and* the anisotropy[11] of the carbon–chlorine bond,[12] rather than the latter alone. Either effect should be enhanced by the close approach of the two atoms;

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[1] Allied Chemical Corp. Fellow, 1962–1963; National Science Foundation Predoctoral Fellow, 1963–1964.

[2] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 112 ff.

[3] 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, p. 137.

[4] Strictly speaking, H_4 is the X part of an ABCX system; however, since H_4 does not appear to be coupled to H_1, ABX is a reasonable description.

[5] L. Crombie and J. W. Lown, *Proc. Chem. Soc.* (London), 299 (1961).

[6] F. A. L. Anet, *Can. J. Chem.*, **41**, 883 (1963).

[7] A. C. Huitric, *J. Org. Chem.*, **27**, 715 (1962).

[8] F. A. L. Anet, *J. Chem. Phys.*, **32**, 1274 (1960).

[9] Varian Associates, "High Resolution NMR Spectra Catalog," Spectrum No. 338.

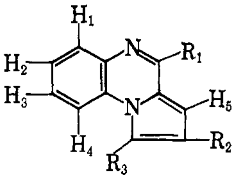
[10] Y. Osawa and M. Neeman, *J. Am. Chem. Soc.*, **85**, 2856 (1963).

[11] Ref. 2, p. 115.

[12] G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.*, **38**, 2736 (1963).

Table I[a]

N.M.R. Spectra of Pyrrolo[1,2-*a*]quinoxalines



Compound	R_1	R_2	R_3	τ-values R_1	R_2	R_3	H_1	H_2	H_3	H_4	H_5
1	C_6H_5	CH_3	H	∽2.5	7.74	2.6–2.8	2.6–2.8	← 2.02 →			3.29
2	CH_3	H	Cl	7.42	3.30	...	2.27	← 2.71 →		1.16	3.43
3	CH_3	CH_3	Cl	7.48	7.91	...	2.30	← 2.75 →		1.20	3.48
4	C_6H_5	H	Cl	2.60	3.17	...	← 2.13 →			1.02	3.38
5	C_6H_5	CH_3	Cl	2.54	7.73	...	← 2.06 →			0.97	3.19

[a] The preparation of these pyrrolo[1,2-*a*]quinoxalines is described elsewhere [E. C. Taylor and G. W. H. Cheeseman, *J. Am. Chem. Soc.*, **86**, 1830 (1964)]; a preliminary account of the synthetic work was presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, Abstracts, p. 70Q.

measurements on models give a Cl–H distance of only 2.27 Å.

The variation of the position of the H_1 resonance is also worthy of attention. In compounds **2** and **3**, where R_1 = methyl, H_1 appears at lower field than H_2 and H_3, reflecting its position *ortho* to nitrogen. In compounds **4** and **5**, however, when R_1 = phenyl, H_1 is shifted to higher field, merging with the H_2–H_3 resonance. We attribute this shift to conjugation of the 1-position with the phenyl group; resonance structures can be written which place a formal negative charge at position 1.

All spectra were obtained on a Varian Associates A-60 spectrometer at normal operating temperature. Compounds were run as *ca.* 10% solutions in reagent grade carbon tetrachloride with 1% tetramethylsilane as internal standard. Chemical shifts are considered accurate to ±1 c.p.s., coupling constants to ±0.1 c.p.s.

Acknowledgment.—We wish to thank Dr. Pierre Laszlo for a helpful discussion. This work was supported in part by research grants to Princeton University from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service (Grant No. CA-02551), and from the American Cancer Society.

Base-Induced Fragmentation of 2-Phenyl-1,3-dioxolane[1]

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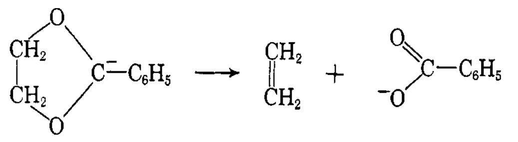
Received February 13, 1964

We wish to report a representative of an unexplored and potentially useful class of reactions: 1,3-eliminations of anionic fragments.[2-4]



2-Phenyl-1,3-dioxolane, treated dropwise with phenyllithium in ether at room temperature, rapidly evolved a gas which was collected (80–94% in three separate runs) and shown to be pure ethylene by mass spectrometry. Formally, the reaction proceeds by 1,3-elimination of benzoate anion from the conjugate base of 2-phenyl-1,3-dioxolane. Although benzoic acid was not recovered from the reaction mixture the observed products are consistent with the elimination of lithium benzoate and subsequent reaction with phenyllithium: from one run benzophenone and triphenylcarbinol were recovered in an over-all yield of 85% based on 2-phenyl-1,3-dioxolane.

Experimental

The reaction vessel, a 250-ml. three-necked round-bottomed flask, was fitted with a gas inlet tube, addition funnel with pressure-equalizing side arm, and a condenser. The condenser was connected to a gas buret *via* two traps cooled in a Dry Ice-acetone mixture and a gas sampling tube. The Dry Ice traps prevented ether vapors from reaching the gas buret and thus facilitated the volumetric and mass spectroscopic determinations of gas evolved in the reaction. The entire system was thoroughly flushed with helium, both before and after adding 4.892 g. (32.6 mmoles) of 2-phenyl-1,3-dioxolane[5] to the reaction vessel and 100 ml. of an ethereal solution of phenyllithium (*ca.* 125 mmoles) to the addition funnel. After allowing the volume of the system to equilibrate (*ca.* 1 hr.) the solution of phenyllithium was added dropwise to the reaction vessel until gas evolution ceased. The reaction mixture was stirred (magnetically) continuously and the reaction vessel was immersed in a bath of water at room temperature. Gas evolution ceased when 17 ml. of phenyllithium solution remained unadded. The increase in volume, 769 ml. at 736 mm. and 22°, corresponded to 94% of the theoretical evolution of 1 equiv. of gas. The mass spectrum of the gas (m/e = 70 to 12) was indistinguishable (±2%) from a mass spectrum of pure ethylene obtained under the same conditions.

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[1] Grateful acknowledgment is made of financial support from the Petroleum Research Fund (Grant 1116-A4).

[2] An interesting and related example was reported by R. L. Letsinger and D. F. Pollart, [*J. Am. Chem. Soc.*, **78**, 6079 (1956)]. They found that treatment of 2-phenyltetrahydrofuran with propyl- or phenyllithium, followed by work-up, yielded ethylene and acetophenone in high yields. Unpublished work with Y. C. Poon has furnished another variation: ethylene glycol sulfite is reduced to ethylene in variable yield (so far not greater than 30%) by metallic sodium or potassium in refluxing xylene.

[3] 1,3-Eliminations of stable and unstable *neutral* molecules are well known and are referred to in the exhaustive documentation of 1,3-additions by R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 565 (1963).

[4] The conversion of 1,2-diols to olefins provides an example of immediate synthetic applicability. *Cf.* E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, **85**, 2677 (1963).

[5] H. Hibbert and J. A. Timm, *ibid.*, **46**, 1283 (1924).