presence of carbonyl impurities, the spectra of the products were not amenable to reliable interpretation. However, when 2 moles of tri-*n*-butyltin hydride were allowed to react with the acid chloride, a 55% yield of phthalide crystallized from the reaction mixture. Its formation undoubtedly results from the reduction of 3-chlorophthalide formed by way of a sequence such as (2). The ready reduction of the phthalide in the second step occurs because the chlorine is now benzylic, and therefore more susceptible to reduction than that in γ-chloro-γ-butyrolactone.

EXPERIMENTAL

Reaction between succinyl dichloride and tri-n-butyltin hydride. To 2.92 g. (18.9 mmol.) of succinyl dichloride which had been freshly distilled was added 5.50 g. (18.9 mmol.) of tri-*n*-butyltin hydride.[6]

The reactants were allowed to stand, with occasional cooling to keep the temperature below about 40°, for 2 hr. Distillation from a modified Claisen flask provided two fractions: b.p. 49–62°/0.3–0.4 mm., 1.84 g. (80%) and b.p. 102–127°/0.4 mm., 6.06 g. (98% crude tri-*n*-butyltin chloride). The first fraction was redistilled yielding a main fraction b.p. 45°/0.4 mm., 1.00 g. of γ-chloro-γ-butyrolactone.

Anal. Calcd. for $C_4H_5O_2Cl$: Cl, 29.4; neut. eq., 60.3. Found: Cl, 28.1, 28.0; neut. eq., 60.5.

Reaction between phthalyl dichloride and tri-n-butyltin hydride. A mixture of 11.0 g. (37.8 mmol.) of tri-*n*-butyltin hydride and 4.54 g. (8.9 mmol.) of phthalyl dichloride was cooled in a water bath occasionally during the first hour after preparation in order to keep the temperature below 50°. It was then allowed to stand for 5 days; 0.47 g. of crystals which had appeared were filtered off and washed with 10 ml., of petroleum ether, b.p. 30–60°. The filtrate was diluted with 20 ml. more of petroleum ether, whereupon another 0.91 g. of crystals appeared. The product melted at 72–74°, undepressed upon mixture with authentic phthalide, and had an infrared spectrum identical with that of phthalide.

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Proton Nuclear Resonance Spectroscopy. X. Rapid Tautomerization of Formazans[1,2]

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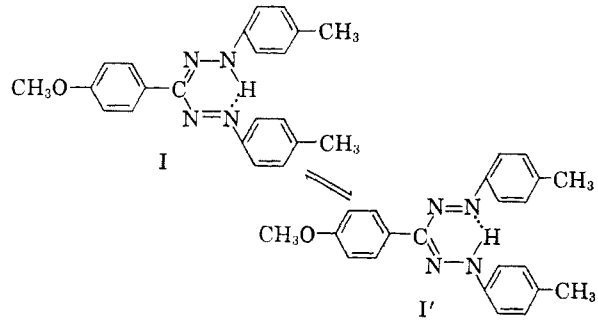
Early workers, studying the problem of tautomerism in unsymmetrically substituted formazans, reported the isolation of two tautomers[4]; however, subsequent studies[5–7] showed that only one form could be isolated. The cyclic hydrogen-bridged structure was proposed[6] in view of the chelating ability of formazans, and the failure to isolate two forms of the chelates prepared from unsymmetrical formazans. In all such studies the requirement of unsymmetrical substitution introduces the possibility of severe steric, electronic, and solvent effects upon the position of tautomeric equilibrium.

Nuclear spin resonance (NSR) spectroscopy affords a sensitive method for the detection of rapid equilibration: it is especially suitable for the study of symmetrical systems,[8] for example, 1,5-di-(4-methylphenyl)-3-(4-methoxyphenyl) formazan



(I). For such purposes it is necessary to choose cases for which all the observed NSR peaks can be assigned with confidence; for the formazan (I) the detailed assignment is given in Table I.

TABLE I

ASSIGNMENT OF NSR SHIELDING VALUES[a] FOR FORMAZAN (I)

Proton Group	Shielding Value, τ (p.p.m.)[a]	Relative No. of Protons
For the 4-Methoxyphenyl Group:		
2-H	2.10[b] | J =	2
3-H	3.20[b] | 8.9c/s	2
4-CH_3O	6.218 ± 0.002	3
For the 4-Methylphenyl Groups:		
2-H	2.59[b] | J =	4
3-H	2.93[b] | 8.5c/s	4
4-CH_3	7.684 ± 0.002	6

[a] For the definition of τ see ref. 10; the formazan, I, concentration was 8% (wt./vol.) in CCl_4. [b] "Nonequivalent doublet" (AB-type) analyzed according to ref. 8, p. 119; the coupling constant J refers to spin interaction between 2- and 3-H.

Whenever NSR assignment may be desired, it is important to avoid unsubstituted phenyl groups, and to synthesize, instead, an appropriate *para*-substituted analog; it may not be widely

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recognized that *only infrequently* do phenyl groups give analyzable NSR patterns. *Para*-substituents having spin $^1/_2$ (F^{19}, P^{31}) introduce some complexity and should be avoided; all others (including D) appear quite satisfactory.

A further advantage is gained in the present instance by the use of "*para*-sensitive" groups such as methyl and methoxy (formyl, acetyl, and dimethylamino also are good) which give sharp NSR peaks, the exact spectral location of which is dependent upon the electrical nature of the structure attached *para* to them.[9] Thus, the 3-position in the formazan appears to be slightly electron-withdrawing, the methoxy shift being −0.048 p.p.m. relative to anisole,[10] while the *average* of the 1- and 5- positions is slightly electron-donating as judged by the positive methyl shift, +0.021 p.p.m., compared to toluene.[10]

The two apparently different *p*-tolyl groups of I in fact yield identical spectral patterns; if a symmetrical, "mesomeric" structure be ruled out, the observed equivalence requires rapid tautomerization, with an estimated lower limit for the rate constant being *ca.* 10^3 sec.$^{-1}$.[8] An alternative explanation, based on rapid intermolecular NH exchange, is excluded, as it would require a sharp NH peak (not seen), the effects of spin-spin interaction and quadrupole broadening by N^{14} being averaged to zero by such exchange.[11]

EXPERIMENTAL

The NSR equipment and techniques used were previously described.[10,12]

1,5-Di-(4-methylphenyl)-3-(4-methoxyphenyl)-formazan (I). A solution of 2.4 g. (0.01 mol.) of *p*-anisaldehyde-*p*-tolylhydrazone in 300 ml. 95% ethanol at 0° was treated with a diazonium salt solution prepared from 1.07 g. (0.01 mol.) *p*-toluidine, 2.5 ml. (0.03 mol.) 12*N* HCl and 0.76 g. (0.11 mol.) sodium nitrite, at 0°. The *p*H of the diazonium salt solution was adjusted to 6.5 by means of sodium acetate, and it was added dropwise to the vigorously stirred hydrazone solution. After 15 min. a yellow solid was filtered from the solution and allowed to stand until its color was deep red; it was twice recrystallized from ethanol, 2.6 g. (73%) being recovered as deep red needles, m p. 172–175° (uncorr.).

Anal. Calcd. for $C_{22}H_{22}ON_4$: N, 15.64%. Found: N, 16.08%.

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The Tetrazole-Azidoazomethine Equilibrium. III. Reduction of Pyridotetrazoles[1]

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The presence of an equilibrium between pyridotetrazole (I) and 2-azidopyridine (III) with electron withdrawing substituents in the pyridine ring was established by spectrophotometric detection of both azido and tetrazolo groups in solutions of certain examples. With no substituent or with electron donating substituents, azide concentration, if present, was not detected.[2] The marked stability of pyridotetrazole in strong acid[3] may be explained by an electromeric displacement toward the electron seeking tetrazole ring. An electromeric displacement toward the pyridine ring, on the other hand, would decrease the stability of the tetrazole ring in I relative to its tautomer III, and might be realized in alkaline solutions.[4] A confirmation of the two possible electronic displacements has been found in catalytic hydrogenation of pyridotetrazole in acidic, basic and neutral media and by reduction of 7-methyl-8-nitropyridotetrazole with stannous chloride in hydrochloric acid.

A detailed catalytic reduction of the tetrazole ring has not been reported heretofore.[5] Its resistance to catalytic hydrogenation was demonstrated in the reduction of I over a noble metal to di- and tetrahydropyridotetrazole[6] (II) and in the reduction of 5-phenyltetrazole in acetic acid over platinum to 5-cyclohexyltetrazole.[7] In the present work, reduction of pyridotetrazole (I) over palladium in the presence of acetic acid to tetramethylenetetrazole (II) in nearly quantitative yield, together with a trace of 2-aminopyridine (IV) has been realized. A dihydropyridotetrazole is not detected. In con-

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(3) Pyridotetrazole is recovered unchanged from concentrated sulfuric acid at 120° (J. H. Boyer, W. J. McCarville, D. I. McCane, and A. T. Tweedie, *J. Am. Chem. Soc.*, **75**, 5298 (1953).

(4) Preliminary observations suggested an instability of pyridotetrazole and its derivatives in bases.[3]

(5) Ring cleavage of tetrazolium salts may occur upon catalytic reduction over palladium [D. Jerchel and R. Kuhn, *Ann.*, **568**, 185 (1950)]. R. O. Roblin, Jr., J. H. Williams, P. S. Winnek, and J. P. English, *J. Org. Chem.*, **62**, 2002 (1940) state that 5-*p*-nitrobenzenesulfonamidotetrazole is reduced over palladium to sulfanilylguanidine, but they do not give the experimental procedure.

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