The Structure of Wallach's Compound, $C_7H_4Cl_9NO_3$

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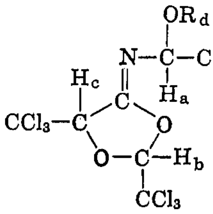
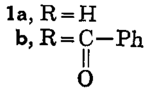
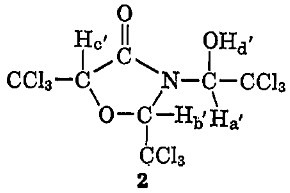
Wallach's compound $C_7H_4Cl_9NO_3$[2] has recently been assigned the lactam structure **2**.[3] On the basis of chemical behavior and infrared and n.m.r. spectral data, we prefer the cyclic imidate structure **1a** to the other possibilities **2**–**6**. The known transformation[3,4] of Wallach's compound to a benzoate **1b** and its subsequent hydrolysis to the amide ester **7** serve to disqualify structures **3**–**6** (barring unlikely benzoyl migration). The claim of Crowther, *et al.*,[4] was confirmed that chloralide (**8**) was the only product other than chloral hydrate isolated from a hydrolysis of Wallach's compound. This observation is better explained by imidate **1a** than by any alternate structure. The absorption in the infrared spectrum at 1745 cm.$^{-1}$ attributed to the iminocarbonyl group in **1a** is at a higher frequency than for any previously reported imine.[5] This can be understood by considering the effect of trichloromethyl groups in known compounds [compare **8**, $\nu_{\max}$ 1850 cm.$^{-1}$ (C═O), to the acetonide of mandelic acid (**9**), $\nu_{\max}$ 1800 cm.$^{-1}$ (C═O)].

Consideration of the n.m.r. spectra of Wallach's compound and its transformation products (Table I) reinforces the assignment of the imidate structure **1a**. The spectra of Wallach's compound **1a** before and after addition of D_2O reveal proton H_a coupled to hydroxyl proton H_d. There are also signals for a pair of protons H_b and H_c which are very similar to those in **8**.[6] This spectrum differs from that predicted for lactam **2** which would place $H_{a'}$ (the hydroxyl-coupled proton) and $H_{b'}$, both deshielded by trichloromethyl, oxygen, and amide nitrogen, at lower field than $H_{c'}$. The proton $H_{c'}$ would be deshielded by trichloromethyl, oxygen, and amide carbonyl (the effect of the last being weaker than that of amide nitrogen by at least 1 p.p.m.[7]). The observed spectra can be accounted for by structure **1a** if (i) the deshielding effect of the iminocarbonyl nitrogen on H_a is less than that of an amide nitrogen (or ester oxygen), and (ii) the deshielding effect of a "chloral"-substituted oxygen on H_c is somewhat greater than that of a hydroxyl oxygen on H_a. If these conditions are met, the upfield position of H_a relative to H_b and H_c is explained. The correspondence of the signals of H_b and H_c to their counterparts in chloralide (**8**) does not require rationalization. From the few spectra of imidates described,[5] it appears that the effect of imino nitrogen is no greater than that of an amine (a smaller effect than that of an amide).[8] This observation satisfies condition i. Further data for satisfaction of these conditions can be obtained by examining spectra of the benzoyl derivative **1b** and the ring-opened amide ester **7**.[9]





1a, R = H
b, R = $\underset{O}{\underset{\|}{C}}-Ph$



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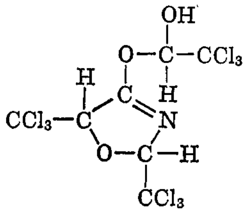

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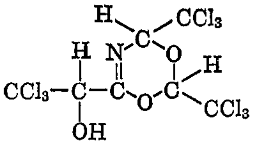

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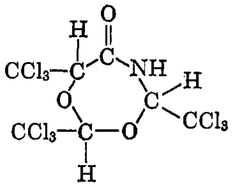

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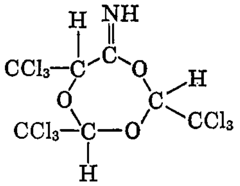

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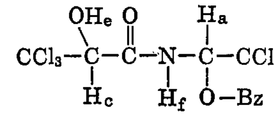
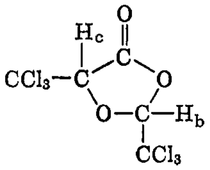


$CCl_3-\underset{H_c}{\overset{OH_e}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H_f}{N}-\underset{O-Bz}{\overset{H_a}{C}}-CCl_3$

7



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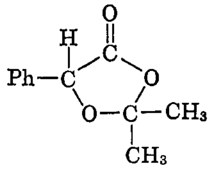

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The spectrum of **1b** reveals the ring protons H_b and H_c slightly shifted and H_a, now deshielded by an ester-like oxygen, shifted downfield by 1.58 p.p.m.[10] Hydrolysis of the benzoate **1b** to the ring-opened structure **7** will now place H_a adjacent to an amide nitrogen (albeit substituted with a hydrogen rather than a deshielding chloral residue) and our rationale requires the observed shift of the H_a signal to lower field. Con-

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[2] O. Wallach, *Ann. Chem.*, **173**, 297 (1874).

[3] R. E. Bowman, A. Campbell, and E. M. Tanner, *J. Chem. Soc.*, 692 (1963).

[4] H. L. Crowther, H. McCombie, and T. H. Reade, *ibid.*, 933 (1914).

[5] H. E. Zaugg, R. W. DeNet, and R. J. Michaels, *J. Org. Chem.*, **28**, 1795 (1963).

[6] N. S. Bhacca, L. F. Johnson, and J. N. Schoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, 1963, No. 425. Compare the values δ 6.09 and 5.12 obtained in carbon tetrachloride to those obtained in dioxane (Table I).

[7] See ref. 6, No. 68 (2-pyrrolidone) and 421 (dimethylacetamide).

[8] See ref. 6, No. 116 (N-methylpyrrolidone) and 269 (nicotine).

[9] We wish to thank a referee for suggesting the use of these spectra in our discussion.

[10] This shift is larger than the value of 1 p.p.m. usually cited when going from a secondary alcohol to an acetate. The present hydroxyl function, however, resembles a hemiacetal with several hydrogen-bonding possibilities. Thus the oxygen is probably more electron rich than in an ordinary alcohol and probably has less deshielding power. Formation of an acyl derivative should therefore cause a greater differential than is ordinarily observed.

TABLE I

N.M.R. SPECTRA OF WALLACH'S COMPOUND AND DERIVATIVES[a]

Compd.	H_a	H_b	H_c	H_d	H_e	H_f	J, c.p.s.
1a	5.47 (d)	6.40 (d)	5.62 (d)	5.93 (d)	...	...	ad, 9 bc, 0.9
1a + D_2O	5.47 (s)	6.40 (d)	5.62 (d)	No peak	...	...	bc, 0.9
8	...	6.42 (d)	5.55 (d)	...	...	...	bc, 1.2
1b[b]	7.05 (s)	6.47 (d)	5.78 (d)	...	...	...	bc, 1.0
7[c]	7.35 (d)	...	4.70 (d)	...	6.32 (d)	8.38 (d)	af, 10 ce, 9
7 + D_2O	7.40 (s)	...	4.76 (s)	...	No peak	No peak	

[a] Spectra were obtained with a Varian A-60 instrument with dioxane as a solvent and are recorded on the δ-scale with tetramethylsilane (δ = 0.0 p.p.m.) as an internal standard; d = doublet, s = singlet. [b] The aromatic protons appeared as two groups centered at 7.67 and 8.17. [c] The coupling of H_a to H_f and H_c to H_e was confirmed in the D_2O exchange experiment when H_e disappeared as H_c merged to a singlet more rapidly than H_f and H_a, respectively. The aromatic protons appeared as two groups centered at 7.68 and 8.18.

versely, hydrolysis of a benzoate of lactam **2**, would require an upfield shift of the signal for $H_{a'}$. The observed downfield shift of H_a in **7** relative to H_a in **1b** is consistent with the structures assigned and with our estimate that an imino nitrogen is not so deshielding as an amide nitrogen. The H_c signal in **7**, being shifted upfield from H_c in **1b**, in **8**, and in **1a** supports the assumption that a "chloral"-substituted oxygen is more deshielding than a hydroxyl.

Thus all the data are consistent with the designation of Wallach's compound as 2,5-bis(trichloromethyl)-N-(1-hydroxy-2,2,2-trichloroethyl)-4-iminodioxolane (**1a**).

Experimental

Melting points were obtained on a Fisher-Johns apparatus and are corrected. Infrared spectra were obtained with a Perkin-Elmer Model 137 instrument using CCl_4 as a solvent.

2,5-Bis(trichloromethyl)-N-(1-hydroxy-2,2,2-trichloroethyl)-4-iminodioxolane (**1a**), Wallach's compound ($C_7H_4Cl_9NO_3$), was prepared as previously described[4] and recrystallized from benzene: m.p. 122–123° (lit.[4] m.p. 122–123°); ν_{max} 1745 cm.$^{-1}$; n.m.r. (dimethyl sulfoxide) δ 5.47 (doublet, J = 7 c.p.s.), 5.98 (doublet, J = 0.8 c.p.s.), 6.72 (doublet, J = 0.8 c.p.s.), and 7.75 (doublet, J = 7 c.p.s.); this last peak was washed out on addition of D_2O.

2,5-Bis(trichloromethyl)-N-(1-benzoyloxy-2,2,2-trichloroethyl)-4-iminodioxolane (**1b**) was prepared as previously described[4] and recrystallized from absolute ethanol: m.p. 142° (lit.[4] m.p. 142°); ν_{max} 1750–1730 cm.$^{-1}$ (broad); n.m.r. (dimethyl sulfoxide) δ 6.28 (doublet, J = 1 c.p.s.), 6.95 (doublet, J = 1 c.p.s.), 7.0 (singlet), complex aromatic absorption 7.68 and 8.15.

N-(1-Benzoyloxy-2,2,2-trichloroethyl)-*α*-hydroxy-*β*,*β*,*β*-trichloropropionamide (**7**) was prepared as previously described[4] and recrystallized from benzene: m.p. 164–167° (lit.[4] m. p. 166°), ν_{max} 1750 and 1710 cm.$^{-1}$. This compound had to be dried at 25° (0.1 mm.) for several hours to remove traces of benzene (as seen by n.m.r. spectroscopy).

Chloralide (**8**).—A solution of 1.00 g. (0.2 mmole) of Wallach's compound in 2 ml. of glacial acetic acid and 1 ml. of concentrated hydrochloric acid was warmed on a steam bath for 2 min. The solution was cooled and the crystallized chloralide was filtered and dried. This procedure afforded 125 mg. (18%) of chloralide, m.p. 112–114°, m.m.p. with authentic chloralide 112–114°.[11] The infrared spectra of both samples were superimposable with strong bands at 1850, 1333, 1266, 1178, 1114, 1032, 1020, 917, and 855 cm.$^{-1}$. Hydrolysis experiments in ether saturated with 10% hydrochloric acid yielded recovered starting material. Experiments in acidic methanol and dioxane solutions resulted in formation only of water-soluble material.

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[11] O. Wallach, *Ann. Chem.*, **193**, 1 (1878).

Inductive Effects on the Position of a Ring-Chain Equilibrium[1]

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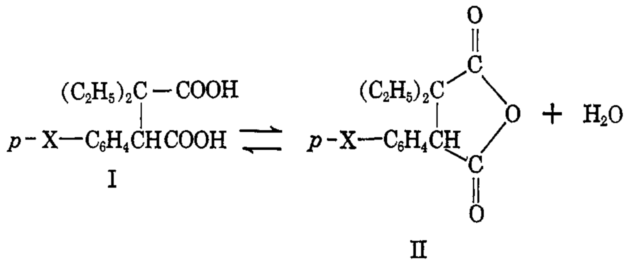
The effect of substitution in favoring the ring form in ring–chain equilibria is a well-recognized but not clearly understood phenomenon.[2] With the objective of quantitatively evaluating the relative importance of bulk *vs.* electronic influences in such equilibria, we have made a Hammett[3] study of the succinic acid–succinic anhydride equilibrium, I ⇌ II. Earlier studies of electronic effects on ring–chain tautomerism in β-bromo-β-benzoyl-*cis*-acrylic acids[4] and α-(β-hydroxyethylamino)deoxybenzoins[5] have demonstrated clearly that complete electronic control of the position of such equilibria is possible through substitutions in the *para* positions of the appropriate benzene nuclei in the compounds, but in both of these cases there was possible direct resonance interaction of the controlling *para* substituent with a carbonyl group immediately involved in a hemiketal type of ring–chain equilibrium. In the compounds we have studied, only an inductive effect is possible, and, as might be expected, the influence of the substituent X is more subtle.



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[1] Taken from the Doctoral Dissertation of K. Tamaribuchi in the Department of Chemistry at Stanford University.

[2] C. K. Ingold and J. F. Thorpe, *J. Chem. Soc.*, 1318 (1928), and earlier papers by these authors; T. C. Bruice and U. K. Pandit, *J. Am. Chem. Soc.*, **82**, 5857 (1960); J. Searles, E. F. Lutz, and M. Tamres, *ibid.*, **82**, 2932 (1960); P. v. R. Schleyer, *ibid.*, **83**, 1368 (1961).

[3] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter 7.

[4] R. E. Lutz and H. Moncure, Jr., *J. Org. Chem.*, **26**, 746 (1961).

[5] C. E. Griffin and R. E. Lutz, *ibid.*, **21**, 1131 (1956).