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 ($\delta = 0.0$ 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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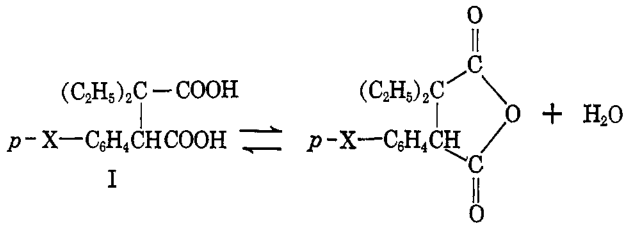
The effect of substitution in favoring the ring form in ring–chain equilibria is a well-recognized but not clearly understood phenomenon.[2] With the objective of quantitatively evaluating the relative importance of bulk *vs.* electronic influences in such equilibria, we have made a Hammett[3] study 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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II

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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).

Experimental

Preparation of Compounds.—The acids I were prepared by hydrolysis of the corresponding methyl 3-cyano-2,2-diethyl-3-*p*-X-phenylpropionates which resulted from condensation of methyl 2-bromo-2-ethylbutyrate with *p*-X-phenylacetonitriles in dimethyl sulfoxide using sodium hydride as base. The condensation proceeded well in all cases except that using *p*-nitrophenylacetonitrile where it failed. Attempts to force the reaction in this case by elevating the temperature resulted in dehydrohalogenation of the bromo ester and polymerization. Typical procedures are described below.

Methyl 2-Bromo-2-ethylbutyrate.—Anhydrous bromine (42 ml.) was slowly added to a stirred mixture of diethylacetic acid (41.5 g.) and phosphorous tribromide (100 g.) over a 2-hr. period. After stirring the reaction mixture overnight, it was added to 100 ml. of absolute methanol at such a rate to maintain reflux. After addition was complete, the solution was heated under reflux for 12 hr., then poured into 100 ml. of ether. Careful extraction of the ether solution several times with saturated sodium bicarbonate solution, drying over anhydrous magnesium sulfate, and distillation yielded 44.8 g. (60% of theory) of methyl 2-bromo-2-ethylbutyrate: b.p. 65–66° (10 mm.), n^{21}_{D} 1.4600, $\nu_{\max}^{\mathrm{film}}$ 1730 cm.$^{-1}$ (CO).

Anal.[6] Calcd. for $C_7H_{13}BrO_2$: C, 40.3; H, 6.3. Found: C, 40.7; H, 6.3.

Methyl 3-Cyano-2,2-diethyl-3-phenylpropionate.—Methyl 2-bromo-2-ethylbutyrate (10.4 g.) and sodium hydride (1.3 g.) were added to 200 ml. of dimethyl sulfoxide previously distilled from calcium hydride. With dry nitrogen protection, 6.0 g. of phenylacetonitrile was introduced during 2 hr. with stirring. The mixture was stirred overnight; the excess sodium hydride was destroyed by adding first 5.0 ml. of methanol and then 250 ml. of water. The aqueous solution was extracted five times with 50-ml. portions of ether; the extract was shaken with six 25-ml. portions of water, dried using anhydrous magnesium sulfate, and distilled to yield 9.6 g. (80% of theory) of methyl 3-cyano-2,2-diethyl-3-phenylpropionate: b.p. 137–138° (0.1 mm.), n^{22}_{D} 1.5079, $\nu_{\max}^{\mathrm{film}}$ 2244 (CN) and 1730 (C=O) cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{19}NO_2$: C, 73.4; H, 7.8. Found: C, 73.5; H, 7.8.

3-Cyano-2,2-diethyl-3-phenylpropionic Acid.—Methyl 3-cyano-2,2-diethyl-3-phenylpropionate (2.5 g.), γ-collidine (80 ml.), and anhydrous lithium iodide (3 g.) were heated under reflux for 12 hr.[7] After decomposition with excess dilute sulfuric acid and extraction with ether, removal of solvent yielded 1.9 g. (82% of theory) of 3-cyano-2,2-diethyl-3-phenylpropionic acid in the form of a viscous, pale yellow oil. On long standing, the oil largely crystallized. Recrystallization from benzene–hexane gave material of m.p.[8] 132.5–133.5° and $\nu_{\max}^{\mathrm{KBr}}$ 2230 (CN) and 1705 (CO) cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.7; H, 7.4. Found: C, 72.6; H, 7.6.

Attempts to carry out the hydrolysis using conventional acidic or basic catalysts failed under even very vigorous conditions.

2,2-Diethyl-3-phenylsuccinic Anhydride (II, X = H).—A solution of 1.5 g. of 3-cyano-2,2-diethyl-3-phenylpropionic acid in 25 ml. of 1:1 hydrochloric acid–acetic acid was heated under reflux for 12 hr. After removal of solvent at reduced pressure the organic material in the residue was taken up in a small volume of ether. To the ether solution was added 5 ml. of acetic anhydride and the mixture was heated on the steam bath under reflux for 3 hr. After extraction with 10 ml. of saturated sodium bicarbonate solution, the ether layer was dried over anhydrous magnesium sulfate and freed of solvent. The oily residue obtained was chromatographed on silicic acid (80 g.) using benzene as eluent to give 0.76 g. of white solid. Sublimation of this solid at 64–65° (10 μ) and crystallization of the sublimate from petroleum ether (b.p. 30–60°) yielded 0.55 g. (36% of theory) of 2,2-diethyl-3-phenylsuccinic anhydride: m.p. 77–78°; $\nu_{\max}^{\mathrm{KBr}}$ 1860, 1840, and 1760 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.4; H, 6.9. Found: C, 72.7; H, 7.0.

For conversion to the acid, 0.13 g. of 2,2-diethyl-3-phenylsuccinic anhydride was warmed with 5.00 ml. of 0.100 *N* sodium hydroxide solution for 12 hr. on the steam bath. The basic solution was cooled, then neutralized with 2.50 ml. of 0.200 *N* hydrochloric acid solution. As the acid was added, white crystals began to separate. Filtration and washing with water, followed by drying at 25° (5 mm.) for 3 hr. gave 0.114 g. (90% of theory) of **2,2-diethyl-3-phenylsuccinic acid (I, X = H)**: m.p. 176–177°, $\nu_{\max}^{\mathrm{KBr}}$ 3430 (OH) and 1705 (CO) cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.2; H, 7.3. Found: C, 67.4; H, 7.4.

When 2,2-diethyl-3-phenylsuccinic acid was exposed to laboratory air during several days its melting point fell. Infrared spectroscopy showed that the acid was undergoing spontaneous conversion to its anhydride.

2,2-Diethyl-3-(*p*-X-phenyl)succinic Acids and Their Anhydrides.—These preparations followed the plan described above for the unsubstituted case. The properties of the compounds and the over-all yields based on the amounts of substituted phenylacetonitriles follow.

2,2-Diethyl-3-(*p*-chlorophenyl)succinic anhydride (17% of theory) had m.p. 63–64°, $\nu_{\max}^{\mathrm{KBr}}$ 1860, 1840, and 1770 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{15}ClO_3$: C, 63.1; H, 5.7. Found: C, 63.2; H, 5.9.

2,2-Diethyl-3-(*p*-chlorophenyl)succinic acid had m.p. 158–160°, $\nu_{\max}^{\mathrm{KBr}}$ 3430 and 1705 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{17}ClO_4$: C, 59.0; H, 6.0. Found: C, 58.8; H, 6.2.

2,2-Diethyl-3-(*p*-methylphenyl)succinic anhydride (12% of theory) had m.p. 73.5–74.5°, $\nu_{\max}^{\mathrm{KBr}}$ 1860, 1830, and 1760 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.1; H, 7.4. Found: C, 73.3; H, 7.5.

2,2-Diethyl-3-(*p*-methylphenyl)succinic acid had m.p. 159–160°, $\nu_{\max}^{\mathrm{KBr}}$ 3400 and 1689 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{20}O_4$: C, 68.2; H, 7.6. Found: C, 68.1; H, 7.6.

2,2-Diethyl-3-(*p*-methoxyphenyl)succinic anhydride (14% of theory) was not obtained crystalline nor entirely free of the corresponding acid; $\nu_{\max}^{\mathrm{film}}$ 1860, 1830, 1760, and 1700 cm.$^{-1}$. Thin layer chromatography showed only two components, one of which had same R_f value as the acid described immediately below which was prepared in 86% yield from the impure anhydride by the method described above.

2,2-Diethyl-3-(*p*-methoxyphenyl)succinic acid had m.p. 155–156°, $\nu_{\max}^{\mathrm{KBr}}$ 1690 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{20}O_5$: C, 64.3; H, 7.2. Found: 64.3; H, 7.1.

Analytical Procedure.—Equilibrations were carried out in dimethyl sulfoxide-d_6 to which had been added a weighed amount of standardized dilute sulfuric acid so that the concentration of mineral acid was 0.02 *M* and that of water was 0.5 *M*. Accurately weighed samples of 0.1–0.2 mmole of the succinic acids and their anhydrides were dissolved in separate 0.400-g. quantities of the dimethyl sulfoxide-d_6–water–sulfuric acid solution and the resulting, homogeneous mixtures were placed in n.m.r. sample tubes and in capillary tubes. The tubes were flushed with nitrogen, the contents were frozen, and the tubes were sealed and placed in a thermostat consisting of a paraffin oil bath heated by refluxing vapors of suitable liquids. The temperature of the bath was monitored with a thermocouple and found constant to better than ±0.5°. Capillary sample tubes from a given acid–anhydride pair were periodically removed, chilled, and opened, and the infrared spectra of films of their contents were obtained. When the spectrum of the contents of the tube originally containing acid was identical with that of the contents of the tube originally containing the corresponding anhydride, equilibrium was judged to have been reached, and the n.m.r. spectra of the samples were measured using a Varian HR-60 spectrometer equipped with an integrator and sample thermostat held at the temperature of the equilibration. Integrated values were obtained by direct reading from a Hewlett-Packard digital voltmeter as well as by inspection of the graphical trace of the integral. The standard deviation over ten integrations, five values obtained by direct reading and five graphically, was 5%. The spectrum of an equilibrium mixture showed benzene ring protons of the anhydride and diacid centered at approximately 7.4 p.p.m.[9]; benzylic proton of diacid at 4.1 p.p.m.; benzylic proton of anhydride at 4.7

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(6) Analyses were performed by Stanford Microanalytical Laboratory.

(7) F. Elsinger, J. Schreiber, and A. Eschenmoser, *Helv. Chim. Acta*, **43**, 113 (1960).

(8) Melting points are not corrected. Infrared spectra were obtained using the Perkin-Elmer Model 421 instrument.

(9) Relative to tetramethylsilane as internal standard at 0.0 p.p.m.

p.p.m.; and a single[10] hydroxyl proton signal near 4 p.p.m. due to OH of water, sulfuric acid, and succinic acid. Utilizing the integrals (average of six integrations) for the benzylic protons of acid and anhydride, and that for the benzene ring protons as an internal standard for the total number of moles of anhydride and diacid, in conjunction with the known gravimetric composition of the sample before equilibration, the values of the mole fraction equilibrium constants, K_X, were calculated. (A refers

$$K_X = \frac{(X_A)(X_{H_2O})}{X_D}$$

to anhydride, D to diacid.) Typical values of K_X obtained in this way as equilibrium was approached from the two sides were I (X = H), 0.27 ± 0.02 *vs.* 0.25 ± 0.02; I (X = CH_3), 0.30 ± 0.02 *vs.* 0.31 ± 0.02; and I (X = Cl), 0.124 ± 0.009 *vs.* 0.117 ± 0.009. In the case of I (X = OCH_3) the equilibrium could not be approached from the anhydride side because of the failure to obtain anhydride free from acid (see Preparation of Compounds).

Results

The constants, K_X, and derived thermodynamic quantities for the equilibria are presented in Table I.

Table I

Equilibrium Data for 2,2-Diethyl-3-(*p*-X-phenyl) succinic Acids and Anhydrides[a]

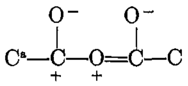
p-X	K_X	$\Delta F°$, kcal./mole	$\Delta\Delta F°$, kcal./mole
CH_3	0.31 ± 0.02	0.87 ± 0.05	−0.13 ± 0.08
H	0.26 ± 0.02	1.00 ± 0.06	0
CH_3O	0.20 ± 0.02	1.19 ± 0.07	0.19 ± 0.09
Cl	0.12 ± 0.01	1.56 ± 0.09	0.56 ± 0.11
Succinic acid[b]	$<10^{-3}$	>5	>4

[a] At 373°K. [b] The limiting values are estimated on the basis that succinic acid under similar conditions was found to exist only in the diacid form within the experimental sensitivity.

Order of magnitude estimates of data for the succinic acid–anhydride equilibrium are included in Table I to set a scale for judging the relative importance of bulk and inductive electronic effects. It is seen that substitution of three of the hydrogens in the chain of succinic acid favors the anhydride form by at least 5 kcal./mole. Since the maximum range of $\Delta\Delta F°$ is only 0.69 kcal./mole, it is clear that the effect of the substituents cannot be purely electronically inductive. The steric or bulk effect is much more important in driving the equilibrium toward the anhydride, a point already established by Lutz[5] in another system. It is also clear from the data in Table I that electron-injecting groups favor the anhydride form.

Although the temperature dependence of K_X was not measured for all compounds, its determination (using the values of K_X at 293 and 373°K.) in the cases of I (X = H) and I (X = Cl) gave the values, respectively, $\Delta H° = 4.9 \pm 0.2$ and 5.5 ± 0.3 kcal./mole and $\Delta S° = 1.05 \pm 0.05$ and 1.05 ± 0.05, giving reassurance that entropy effects are not an important part of the effect of the *para* substituent in changing the position of equilibrium.

While any theoretical explanation for the effect of electron-donating *p*-X substituents is fraught with danger because the data only show an increase in relative stability of the anhydrides with electron-donating *p*-X substituents, it seems not unreasonable to focus attention on effects of electron donation on the stability of the anhydride form, assuming that the substituent has little effect on that of the diacid.[11] Anhydrides are electrophilic reagents, Lewis acids in the sense of the contributing structure



$$C^a-\underset{+}{\overset{\overset{O^-}{|}}{C}}-\underset{+}{O}=\overset{\overset{O^-}{|}}{C}-C$$

and electron density increase in the vicinity of C^a would be expected to diminish the $^+C–O^-$ bond moment with resultant decrease in the energy resulting from unfavorable juxtaposition of bond dipoles. The data may be taken to support such an interpretation.

Acknowledgment.—The authors are indebted to the National Science Foundation (G9476) and the Air Force Office of Scientific Research (AFOSR 62-116 and AF49-638-1272) for their generous support of this investigation. We also wish to express our great appreciation to Dr. Lois J. Durham of these laboratories for her help with the proton magnetic resonance spectral analyses.

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[10] Rapid exchange of hydroxyl protons in the strongly acidic medium is responsible for the single OH signal: J. D. Roberts, "Nuclear Magnetic Resonance. Applications to Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 4.

[11] The fact that the equilibria were established in a medium 0.02 *M* in sulfuric acid removes ionization of the acid as a factor for consideration.

Oxidation of β-Pinene with Lead Tetraacetate[1]

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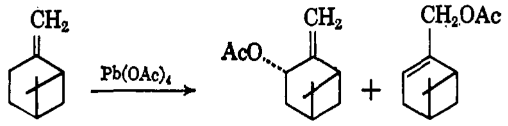
The oxidation of β-pinene (I) with lead tetraacetate in benzene and in acetic acid leads to formation of two monoacetate products in significant amount. These have been identified as *trans*-pinocarvyl acetate (II) and myrtenyl acetate (III).



I II III

The oxidation in acetic acid at 60° was previously carried out by Matsubara,[2] and he reported the monoacetates to be myrtenyl acetate (9% yield based on unrecovered β-pinene) and perilla acetate (4%). In this study, however, we have found that the two major monoacetates formed in the β-pinene oxidation in acetic acid at room temperature are myrtenyl acetate (12%) and *trans*-pinocarvyl acetate (10%). Distillation of all volatile components of the product mixture followed by gas chromatography studies of the fractions revealed that the acetic acid oxidation system is complex and many higher boiling products are formed. Careful duplication of Matsubara's

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[1] Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964.

[2] Y. Matsubara, *J. Chem. Soc. Japan*, **75**, 894 (1954); *Chem. Abstr.*, **49**, 9568e (1955).