Reaction of diallylmercury with thiophenol. To 5.66 g. of diallylmercury[3] (0.02 mole) was added dropwise at room temperature 2.20 g. of thiophenol (0.02 mole). After the exothermic reaction had subsided, the mixture was heated on a steam bath for 0.5 hr. The solid, grey reaction mixture was extracted with an excess of hot acetone, leaving 1.14 g (28.5%) of metallic mercury. On cooling, white needles separated from the acetone solution, 2.76 g. (66%). After recrystallization, the mercury-bis-thiophenolate melted at 154–155° (lit.[1] m.p. 155–156°). Distillation of the acetone mother liquor yielded 0.84 g (28%) allyl phenyl sulfide, b.p. 47–48° at 0.3 mm, n_D^{20} 1.5755 (lit.[4] b.p. 59–60° at 1.5 mm, n_D^{20} 1.5760). The infrared spectrum was identical with the one published by Tarbell and McCall.[4]

Reaction of bis(3-butenyl)mercury with thiophenol. Equimolar amounts of bis(3-butenyl)mercury and thiophenol treated under identical conditions as described above, gave 80% mercury-bis-thiophenolate, m.p. 153.5–154°. and 9% 3-butenyl phenyl sulfide. The infrared spectrum of the latter was identical with the one obtained from an authentic sample.

3-Butenyl phenyl sulfide was prepared in 70% yield from potassium thiophenolate and 1-chloro-3-butene in ethanol according to Ipatieff *et al.*,[12] b.p. 85.5–86.5° at 1.5 mm, n_D^{20} 1.5645.

Anal. Calc. for $C_{10}H_{12}S$: C, 73.12; H, 7.36; S, 19.46. Found: C, 73.24; H, 7.25; S, 19.30. Major infrared absorption bands: 3.25, 3.41, 6.10, 6.75, 6.95, 7.82, 8.20, 9.18, 9.38, 9.77, 10.12, 10.95, 13.59, and 14.51 μ.

A small amount of 1,4-bis(phenylmercapto)butane,[13] m.p. 85–86°, was formed as a by-product in this reaction.

3-Butenyl phenyl sulfone was obtained in 60% yield by oxidizing 3-butenyl phenyl sulfide with hydrogen peroxide according to Pomerantz and Connor,[14] b.p. 120–122° at 0.3 mm, n_D^{20} 1.5404.

Anal. Calculated for $C_{10}H_{12}O_2S$: C, 61.19; H, 6.16; S, 16.34. Found: C, 61.00; H, 6.13; S, 15.99. The infrared spectrum of the compound exhibits the two characteristic —SO_2— absorptions at 7.55 and 8.68 μ.

SOUTH CHARLESTON, W. VA.

---

(12) V. N. Ipatieff, H. Pines, and B. S. Friedman, *J. Am. Chem. Soc.*, **60**, 2732 (1938).

(13) G. McD. Bennet and A. N. Mosses, *J. Chem. Soc.*, 2364 (1930).

(14) A. Pomerantz and R. Connor, *J. Am. Chem. Soc.*, **61**, 3388 (1939).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

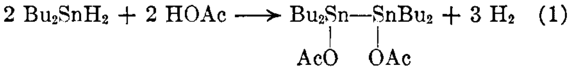
Mechanistic Aspects of the Reaction of Di-*n*-butyltin Dihydride with Acetic Acid[1]

ALBERT K. SAWYER AND HENRY G. KUIVILA

Received August 30, 1961

When di-*n*-butyltin dihydride and di-*n*-butyltin diacetate are mixed, a reaction occurs leading to an equilibrium mixture of these two compounds and di-*n*-butylacetoxytin hydride.[2] This same equilibrium mixture, along with one mole of hydrogen, is formed when one mole of di-*n*-butyltin dihydride is allowed to react with one mole of acetic acid. When the equilibrium mixture is allowed to stand, hydrogen is involved and 1,1,2,2-tetra-*n*-butyl-1,2-diacetoxyditin is formed. It reacts with acetic acid to produce di-*n*-butyltin diacetate.

In a previous investigation[3] it was found that di-*n*-butyltin dihydride reacts with acetic acid to give either of two products as shown in Equations 1 and 2.



$$2\ Bu_2SnH_2 + 2\ HOAc \longrightarrow \underset{AcO}{\underset{|}{Bu_2Sn}}-\underset{OAc}{\underset{|}{SnBu_2}} + 3\ H_2 \quad (1)$$

$$Bu_2SnH_2 + 2\ HOAc \longrightarrow Bu_2Sn(OAc)_2 + 2\ H_2 \quad (2)$$

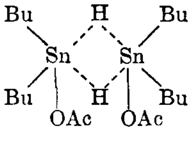
1,1,2,2-Tetra-*n*-butyl-1,2-diacetoxyditin is the main product when the acid-hydride ratio is 1.0, and di-*n*-butyltin diacetate is the major product when the acid-hydride ratio is 2.0. With diphenyltin dihydride, on the other hand, irrespective of whether the acid-hydride ratio is 1.0 or 2.0, the main product is 1,1,2,2-tetraphenyl-1,2-diacetoxyditin. Parallel behavior is observed when other carboxylic acids are allowed to react with these hydrides. It appeared to be of interest to examine the reactions involving di-*n*-butyltin dihydride and acetic acid in detail in order to gain some understanding regarding their mechanisms.

A starting point was provided by the discovery that 1,1,2,2-tetra-*n*-butyl-1,2-diacetoxyditin could be prepared by the reaction of di-*n*-butyltin dihydride with di-*n*-butyltin diacetate as shown in Equation 3. (It was also observed that the analogous reaction could be carried out with di-*n*-

---

(1) Support of this work by Metal and Thermit Corporation is gratefully acknowledged.

(2) For the purpose of this paper, the new tin hydride species, showing Sn—H absorption at 1880 cm.$^{-1}$, is assumed to be di-*n*-butylacetoxytin hydride. This is the simplest structure consistent with its analysis and properties, and the one which involves the least structural change. Other species which would have the same empirical formula include polar species such as Bu_2Sn^{++} $Bu_2Sn(OAc)_2H_2^{--}$, and bridged structures such as



(3)(a) A. K. Sawyer and H. G. Kuivila, *J. Org. Chem.*, *in press*. (b) A. K. Sawyer and H. G. Kuivila, *J. Am. Chem. Soc.*, **82**, 5958 (1960).

Fig. 1. Infrared spectrum of di-*n*-butylacetoxytin hydride at room temperature

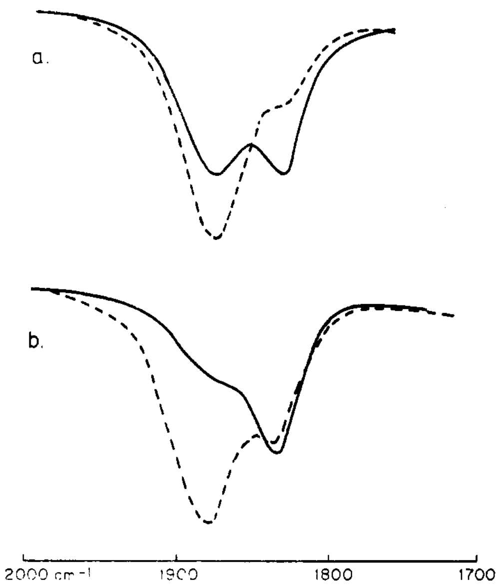
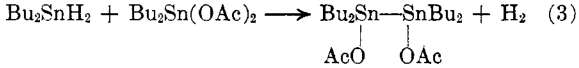


Fig. 2. Infrared spectra of change of di-*n*-butylacetoxytin hydride equilibrium with temperature

a. At 28% hydrogen evolution
b. At 47% hydrogen evolution
——— From reaction mixtures at room temperature
-------- After cooling in bath for 10 minutes



$$Bu_2SnH_2 + Bu_2Sn(OAc)_2 \longrightarrow \underset{AcO}{Bu_2Sn}-\underset{OAc}{SnBu_2} + H_2 \quad (3)$$

butyltin dibenzoate and di-*n*-butyltin succinate). Closer examination revealed that this reaction proceeds in two stages, the first of which is complete within a few minutes and leads to the isolation, after several recrystallizations from ether at −70°, of a colorless solid whose tin and hydride hydrogen analyses correspond to those expected for di-*n*-butylacetoxytin hydride. Examination of the infrared spectrum of the reaction mixture (Fig. 1) reveals two tin-hydrogen stretching frequencies: one at 1835 cm.$^{-1}$, characteristic of di-*n*-butyltin dihydride, and another at 1880 cm.$^{-1}$ which is assigned to di-*n*-butylacetoxytin hydride. The shift to higher frequencies is the expected result of replacing a hydrogen on the tin atom by

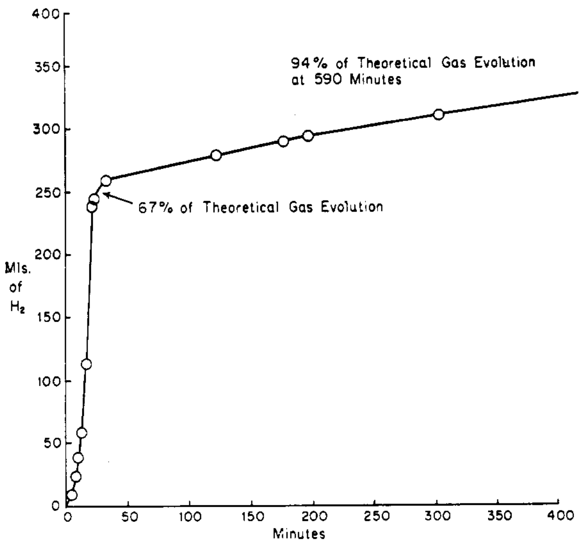
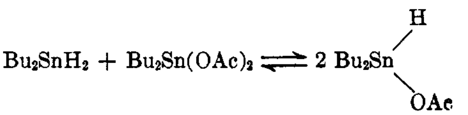


Fig. 3. Plot of gas evolution *vs.* time for the reaction of di-*n*-butyltin dihydride with acetic acid in a 1:1 mole ratio

the more electronegative acetoxy group. Furthermore, upon mixing the reactants, in addition to the carbonyl absorption bands characteristic of di-*n*-butyltin diacetate, new bands appear at 1560 cm.$^{-1}$ and 1415 cm.$^{-1}$ which are assumed to be carbonyl absorptions for the acetoxytin hydride. The existence of a mobile equilibrium between the dihydride and the acetoxytin hydride is revealed by the spectra in Fig. 2. The solid curve in Fig. 2a represents a portion of the spectrum of a reaction mixture which had reacted according to Equation 3 to the extent of 28% as determined by hydrogen evolution. The sample cell was then cooled to about −50° for eleven minutes and the same spectral region scanned, giving the broken curve. Another scan, after the cell had warmed to room temperature, gave a curve similar to the solid curve. Fig. 2b shows the same behavior at a later stage of reaction 3. The equilibrium clearly favors the putative acetoxytin hydride at low temperatures.

The existence of the mobile equilibrium raises the question of whether the solid isolated was actually the acetoxytin hydride or a mixture of it and the reactants. Two additional facts are pertinent. First, the solid was isolated after several recrystallizations. It is most unlikely that a mixture would retain the same stoichiometry under these circumstances. Second, the solid melted at 17–20°, whereas di-*n*-butyltin dihydride is a liquid at room temperature, showing no tendency to solidify when kept for days at 0°, and di-*n*-butyltin diacetate melts at 8.5–9.0°.[3a] It is thus clear that a new compound is at hand, and the most reasonable structure, though not the only one consistent with the facts, is the one stated in Equation 4.



$$Bu_2SnH_2 + Bu_2Sn(OAc)_2 \rightleftharpoons 2\,Bu_2Sn\begin{matrix}H\\ \\OAc\end{matrix} \quad (4)$$

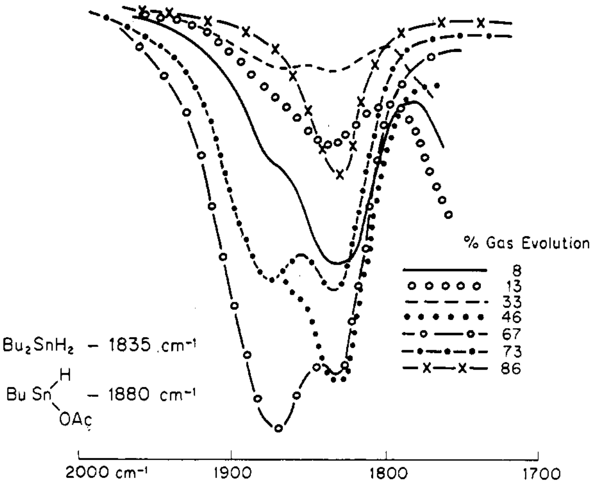
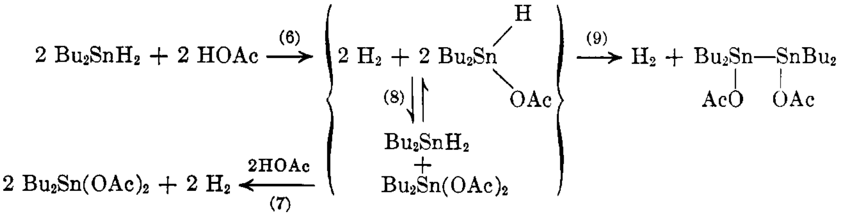


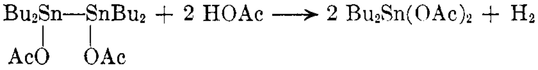
Fig. 4. Infrared spectra for the reaction mixture from di-*n*-butyltin dihydride and acetic acid in a 1:1 mole ratio at various stages in the reaction

The second stage of reaction 3 consists of a relatively slow reaction from which ditin and hydrogen are obtained as products.



The reaction of di-*n*-butyltin dihydride and acetic acid in a 1:1 mole ratio was then examined. The evolution of hydrogen as a function of time for one reaction is shown in Fig. 3. There appears to be a rapid evolution up to 67% followed by a much slower, and rather steady, formation of gas to the end of the reaction. Infrared spectra taken at various stages of gas evolution in several reactions are shown in Fig. 4 and indicate an increase in the $Bu_2Sn(H)OAc/Bu_2SnH_2$ ratio as the reaction proceeded up to 67% gas evolution. At this point the spectrum is identical to that of the mixture of the reactants of Equation 4 at room temperature as shown by comparing Fig. 1 with Fig. 4. From this point on the changes in spectra are similar to those observed for the formation of the 1,2-diacetoxyditin from di-*n*-butylacetoxytin hydride, as can be seen by comparing the spectra at room temperature from the reaction mixtures in Fig. 2 with the spectra after 67% gas evolution in Fig. 4.

In order to make possible spectral examination, a slower reaction was carried out by diluting the reactants with *n*-hexane. The plot of gas evolution *vs.* time, shown in Fig. 5, has the same break in the curve at 67% gas evolution as was observed without solvent. Twelve spectra taken over the course of the reaction showed no evidence for the presence of di-*n*-butylacetoxytin hydride. A carbonyl absorption band at 1607 cm.$^{-1}$, characteristic of di-*n*-butyltin diacetate, appeared early in the reaction, increased to a maximum at about 67% reaction, then decreased in intensity and disappeared at the end. A carbonyl absorption band, characteristic of 1,1,2,2-tetra-*n*-butyl-1,2-diacetoxyditin at 1553 cm.$^{-1}$ began to appear at about 67% reaction and increased in intensity throughout the remainder of the reaction. Only bands characteristic of the 1,2-diacetoxyditin remained at the end. The appearance of the bands characteristic of di-*n*-butyltin diacetate suggests strongly that it is formed *before* 1,1,2,2-tetra-*n*-butyl-1,2-diacetoxyditin. In other words, the simple diacetate is not formed by Equation 5.

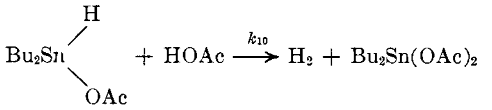


$$\underset{AcO}{Bu_2Sn}\text{—}\underset{OAc}{SnBu_2} + 2\,HOAc \longrightarrow 2\,Bu_2Sn(OAc)_2 + H_2 \quad (5)$$

Confirmation of this conclusion was provided by the fact that when a mixture of 1,1,2,2-tetra-*n*-butyl-1,2-diacetoxyditin and acetic acid were allowed to stand for an extended period of time, no gas evolution occurred.

The above reaction scheme is believed to be consistent with all of the observations presented thus far.

The plot in Fig. 3, combined with the observation that an infrared spectrum identical to that in Fig. 1 is obtained within two minutes of mixing equimolar quantities of di-*n*-butyltin dihydride and di-*n*-butyltin diacetate, shows that reaction 6 is slow compared with reaction 8, forward and reverse. Reaction 9 is even slower, as shown by the plots in Fig. 3 and 5. Furthermore, since the presence of two moles of acid per mole of hydride leads to formation of di-*n*-butyltin diacetate as the product, reaction 9 must also be slower than 7. This question may now be asked: Does di-*n*-butyltin diacetate form only through reactions 6 and 8, or does it involve the sequence 6, 8, 7? In other words, which is larger, k_6 (Bu_2SnH_2) or k_{10} $Bu_2Sn(H)OAc$? Figure 6 shows initial rates of gas evolution in



(10)

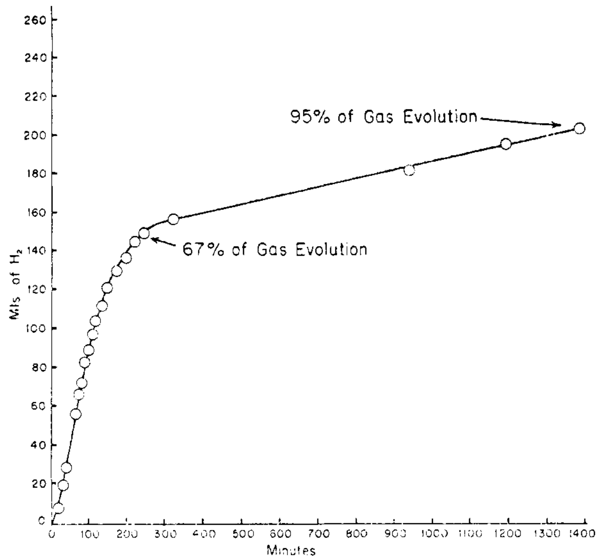


Fig. 5. Di-*n*-butyltin dihydride and acetic acid in a 1:1 mole ratio in *n*-hexane

three reactions using *n*-hexane as solvent. The fact that the slope of the reaction with an acid-hydride ratio of 2.0 is twice that in which this ratio was 1.0 indicates that the reaction is first order in acid. The infrared spectra indicate that acetoxytin hydride does not appear in these reactions, implying that equilibrium 8 lies strongly on the side of dihydride and diacetate. A reaction mixture containing these species and acetic acid, each in 1.52 molal concentration therefore, should give an initial slope equal to half that of a mixture containing 3.04 molal acetic acid and 1.52 molal dihydride if $k_6(\mathrm{Bu_2SnH_2})$ is greater that $k_{10}(\mathrm{Bu_2Sn(H)OAc})$. The fact that this ratio is greater than 0.5 (actually about 0.61) suggests that reaction 10 is involved, at least to some extent, in the formation of di-*n*-butyltin diacetate. Furthermore, as the concentration of the acetoxytin hydride is so small as to be undetectable in the infrared, it follows that k_{10} is much larger than k_6.

EXPERIMENTAL

All melting points are uncorrected.

Tin analyses were carried out by the method of Gilman and Rosenberg.[4] Other analyses were performed by the Galbraith Microanalytical Laboratories, Knoxville, Tenn.

A nitrogen atmosphere was used to protect solutions containing hydride.

Infrared spectra were determined with a Perkin-Elmer Model 21, recording double beam spectrophotometer with sodium chloride optics. Unless otherwise noted all samples were run as liquid films.

Di-n-butylacetoxytin hydride. To 2.91 g. (0.0124 mole) of di-*n*-butyltin dihydride was added 4.35 g. (0.0124 mole) of di-*n*-butyltin diacetate. Within one minute small bubbles of gas appeared and the flask became quite warm. After 2 to 3 min. the flask and its contents were cooled to −70°, whereupon the liquid solidified. The solid was then melted and subsequently recrystallized from 10 ml. of anhydrous ether at −70°. The supernatant liquid was decanted, the solid was washed with 5 ml. of anhydrous ether and the decantate and washings were combined (A). The residue was evacuated to 0.5 mm. as it warmed to room temperature and melted. It was then refrozen and remelted twice under vacuum to give 3.74 g. (52%) of di-*n*-butylacetoxytin hydride, a colorless liquid at room temperature, n_D^{26} 1.4870; m.p. 17–20°.

Anal. Calcd. for $C_{10}H_{22}O_2Sn$: Sn, 40.51; hydride H, 0.34. Found: Sn, 40.60, 40.68; hydride H, 0.33.

An infrared spectrum taken within a few minutes of melting is shown in Fig. 1. The strong band at 1880 cm.$^{-1}$ is most probably the Sn—H band of di-*n*-butylacetoxytin hydride. The solvent from the decantate and washings (A) was removed at 0.5 mm. and low temperature, and the product was melted and refrozen several times as before. The final product was identical to the analytical sample with respect to melting point, index of refraction, and infrared spectrum.

Effect of temperature change on di-n-butylacetoxytin hydride. As the presence of the Sn—H band at 1835 cm.$^{-1}$ at room temperature suggested the possibility of the equilibrium of Equation 4, this was investigated by preparing di-*n*-butylacetoxytin hydride and by observing the changes in its infrared spectrum with temperature at different stages in its decomposition to ditin by reaction 9. In some cases the initial spectrum was taken at room temperature and subsequent spectra were run as rapidly as possible over the 1700–2000 cm.$^{-1}$ range after cooling of the entire assembly containing the sample for successively longer intervals in a Dewar flask containing Dry Ice between spectra. Typical results are shown in Fig. 2. In other cases, the sample was first cooled and then successive spectra were taken as it warmed to room temperature. It was observed that, as the decomposition of the acetoxytin hydride proceeded and its concentration therefore decreased, the ratio of di-*n*-butyltin dihydride to di-*n*-butylacetoxytin hydride increased.

Reaction of di-n-butyltin dihydride with acetic acid in a 1:1 mole ratio. As the reaction occurred too rapidly to take as many spectra as was desired during a single reaction, several runs were made using equimolar quantities of di-*n*-butyltin di-hydride and glacial acetic acid. In one run

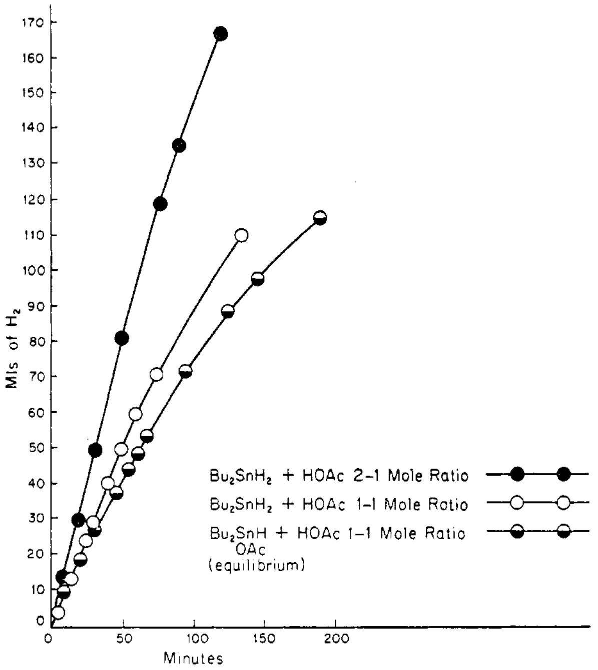


Fig. 6. Initial rates of gas evolution in *n*-hexane at 25°

---

[4] H. Gilman and S. D. Rosenberg, *J. Am. Chem. Soc.*, **75**, 3592 (1953).

when 2.35 g. (0.0100 mole) of di-*n*-butyltin dihydride was mixed with 0.60 g. (0.1000 mole) of acetic acid the rate of gas evolution followed and infrared spectra were taken at 31%, 67%, 78%, and 100% of gas evolved. (The graph of gas evolution *vs.* time for this run is shown in Fig. 3.) The yield of gas obtained in these runs ranged from 95% to 98%.

Reaction of di-n-butyltin dihydride with acetic acid in 1:1 mole ratio in n-hexane. To 1.18 g. (0.0050 mole) of di-*n*-butyltin dihydride was added 5.0 ml. of *n*-hexane followed by 0.30 g. (0.0050 mole) of glacial acetic acid. A graph of gas evolution *vs.* time is shown in Fig. 5. Twelve infrared spectra taken throughout the course of the reaction revealed no trace of the Sn—H band for di-*n*-butylacetoxytin hydride at 1880 cm.$^{-1}$ Further study of the carbonyl absorption region of these spectra showed that di-*n*-butyltin diacetate appeared very early in the reaction, reached a maximum, and was not present at the end. 1,1,2,2-Tetra-*n*-butyl-1,2-diacetoxyditin on the other hand appeared at about 67% gas evolution and was the only species present at the end. Subsequently, 0.0050 mole of di-*n*-butylacetoxytin hydride was prepared from di-*n*-butyltin dihydride and di-*n*-butyltin diacetate and quickly diluted with 5.00 ml. of *n*-hexane. An infrared spectrum, taken immediately thereafter, showed no trace of the Sn—H band at 1880 cm.$^{-1}$ but did show a strong band for di-*n*-butyltin dihydride at 1832 cm.$^{-1}$. The large carbonyl absorption band originally present at 1560 cm.$^{-1}$ had been replaced by a band at 1607 cm.$^{-1}$ which is characteristic of di-*n*-butyltin diacetate. When di-*n*-butylacetoxytin hydride was prepared as above and diluted with an equal volume of ethyl acetate, only a faint suggestion of the band at 1880 cm.$^{-1}$ remained along with a strong band at 1832 cm.$^{-1}$

Determination of the initial slopes of the reactions. To solutions containing 0.0050 mole of hydride species in *n*-hexane (0.152 molal) was added the appropriate amount of acetic acid and 0.1 g. of Norit (which has been found to eliminate the initial lag in gas evolution which has often been observed in these reactions).[5] The mixture was placed in a constant temperature bath at 25° and gas evolution was measured at intervals. These data, for reactions of di-*n*-butyltin dihydride with acetic acid in both 2:1 and 1:1 mole acid-hydride ratios and for the di-*n*-butylacetoxytin hydride equilibrium with acetic acid in a 1:1 mole acid-hydride ratio with acetic acid, are shown in Fig. 7.

DURHAM, N. H.

---

(5) M. S. Newman and E. G. Caflisch, Jr., *J. Am. Chem. Soc.*, **80**, 862 (1958).

[CONTRIBUTION NO. 1636 FROM STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Electron Exchange Polymers. XVIII. Selective Reactivity of *n*-Butyllithium on 1,4-Dimethoxy-2,3,5-trimethylbenzene[1,2]

KENNETH A. KUN[3] AND HAROLD G. CASSIDY

Received October 20, 1961

When 1,4-dimethoxy-2,3,5-trimethylbenzene (I) is reacted with *n*-butyllithium, and then treated with acetaldehyde, the major product is 1,4-dimethoxy-2,5-dimethyl-3β-hydroxy-propylbenzene, the lithium having attacked the benzylic hydrogen of methyl group 3, rather than the aromatic hydrogen in position 6. On dehydration of this secondary alcohol there is produced 2,3-dihydro-5-methoxy-2,4,7-trimethylbenzofuran. In the reaction of I with *n*-butyllithium there is also produced a small amount of the pseudocumohydroquinone monomethyl ether: 1-methoxy-4-hydroxy-2,3,5-trimethylbenzene. These substances are characterized, and directions for their preparation are given along with properties and preparations for the compounds 1,4-dimethoxy-2,5-dimethyl-3-chloro-methylbenzene and 1,4-dimethoxy-2,5-dimethyl-3-deuteromethylbenzene.

During our study of methylated vinylhydroquinones,[4] as monomers for preparing electron exchange polymers (redox polymers), an interesting reaction was observed between 1,4-dimethoxy-2,3,5-trimethylbenzene (I) and *n*-butyllithium. When treated at 0° in ether, then with acetaldehyde, there were obtained two products: a viscous oil boiling between 119 and 125° at 0.5 mm. (II), and a crystalline material melting at 101–102° (III). The homogeneity of the oil was indicated by a single zone in a vapor phase chromatogram (detergent column) and sharp peaks in its NMR spectrogram. Its formula corresponded to $C_{13}H_{20}O_3$ and showed a strong hydroxyl group in the infrared absorption region. Attempts to dehydrate this alcohol under mild conditions such as distilling from fused potassium acid sulfate,[5] refluxing in dried toluene containing catalytic quantities of sulfuric acid or *p*-toluenesulfonic acid, refluxing in glacial acetic acid with dry hydrogen chloride[6] were unsuccessful. Heating the alcohol at 100° with several drops of concentrated sulfuric acid gave a product melting at 49–50° on purification. This substance (IV) contains by microanalysis one methoxyl group, by infrared an aromatic system with no hydroxyl group. Its formula was $C_{12}H_{16}O_2$, having lost water and a methylene group.

Comparison of the NMR spectra of 1,4-dimethoxy-2,3,5-trimethylbenzene (I) (spectrum

---

(1) This paper is taken from the dissertation submitted by Kenneth A. Kun to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) For previous papers in this series see K. A. Kun and H. G. Cassidy, *J. Org. Chem.*, 26, 3223 (1961).

(3) Present address: Rohm & Haas Co., Research Laboratories, Bristol, Pa.

(4) K. A. Kun and H. G. Cassidy, *J. Polymer Sci.*, *in press.*

(5) C. G. Overberger and J. H. Saunders, *Org. Synthesis*, Coll. Vol. III, 204 (1955).

(6) K. A. Kun and P. E. Spoerri, *J. Am. Chem. Soc.*, **77**, 4676 (1955).