hydride reagent. After about 1 min. at room temperature several drops of concentrated hydrochloric or sulfuric acid are added. The color develops at once or after very brief warming. Plant extracts containing leucoanthocyanins give similar colors on addition of hydrochloric acid without the use of sodium borohydride.

Extraction of Douglas fir bark. The powdered bark (50 g.) was extracted in a Soxhlet apparatus first with ether and then with methanol. The methanolic extract was treated with lead acetate; the precipitated lead salts were washed with methanol and decomposed with hydrogen sulfide in methanol. Filtration followed by evaporation of the filtrate yielded a crude crystalline material which was used for paper chromatography.

Chromatography of Douglas fir bark flavonoids. Ascending chromatograms were prepared using 10% acetic acid on Whatman No. 1 paper. After treatment with sodium borohydride and hydrogen chloride three spots were observed: a small purple spot (R_f = 0.29), a large tan spot (R_f = 0.48) (dihydroquercetin) and a bright yellow spot near the origin (R_f = 0.04) (probably quercetin and other flavones). All the spots gave intense reduction of ammoniacal silver nitrate. Eriodictyol had R_f = 0.29 when run simultaneously.

Acknowledgment. I should like to thank Prof. H. Erdtman for a gift of pinocembrin and Mr. Bruno Gentili for the preparation of several of the compounds.

FRUIT AND VEGETABLE CHEMISTRY LABORATORY
WESTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION
AGRICULTURAL RESEARCH SERVICE
U. S. DEPARTMENT OF AGRICULTURE
PASADENA, CALIF.

Solvation of Stilbene and Azobenzene Metal Adducts

WALTER BOOS AND GEORGE F WRIGHT

Received May 20, 1957

The addition of alkali metals to unsaturated compounds is facilitated by inclusion of ether in which the adducts are soluble. Little is known about the chemical effects of these ethers. In one instance stable etherates are reported[1] and in another instance an optically active ether has conferred activity to the product from an adduct.[2] Now we have studied the etherates of stilbene and azobenzene metal adducts, which remain after evaporation of dioxahexane solutions.

The sparingly-soluble azobenzene dilithium adduct in 2,5-dioxahexane has been shown to undergo a variety of alkylation reactions.[3] We have confirmed the behavior by preparation from 1-chlorobutane of *N*,*N*′-di-*n*-butylhydrazobenzene. In order to ascertain the role of the dioxahexane in these metal-adducts systems we have heated the azobenzene-dilithium suspension both at 50° (30 mm.) and also at 100° (5 mm.). In either instance the dry residue has the same yellow color it displays in the suspension. When a weighed amount of this dry diadduct is hydrolyzed by water and then is analyzed for lithium content, the calculated formula weight indicates that 2 molecules of dioxahexane are coordinated with 1 molecule of azobenzene dilithium. Indeed, we have isolated 95% of the 2,5-dioxahexane expected if each lithium atom were coordinated with both oxygens of such a diether. Of interest is the further observation that the azobenzene disodium adduct also is coordinated with 2 molecules of dioxahexane.

If the rate of alkylation of the dimetal adducts is dependent on coordination interchange between the ether and the alkylating agent, then the more reactive stilbene-disodium ought to be less firmly solvated than its azobenzene analogue. But experiment shows that vacuum-evaporation of the stilbene-disodium system at 25° leaves a red residue in which 2 molecules of dioxahexane are included. However, the similarity with the azobenzene disodium adduct no longer prevails when the stilbene-disodium adduct is heated under vacuum at 50° or 100°. Then the ratio is found by titration for alkali to correspond with 2 molecules of adduct per one molecule of dioxahexane.

This evidence that solvation is less firm to the carbon-sodium linkage than it is to the nitrogen-sodium linkage is exemplified further by the observation that the stilbene-disodium containing only one ether-oxygen per two atoms of metal is more active than disodium adduct in which one atom of metal is coordinated with two ether-oxygen atoms. Thus it reacts more rapidly with alkylation agents.

It is of further interest to discover whether the diastereomeric ratio of dialkylation products from stilbene-disodium adducts is altered by the extent of solvation. An alkylation agent must be chosen for which the reaction rate is sufficiently slow that interphase reactivity is minimized in the heterogeneous systems comprising the several solvated species. We have chosen diethyl sulfate which is known to react slowly with the solution of stilbene-disodium adduct in dioxahexane to give 13% of *meso* and 26% of *dd,ll*-3,4-diphenylhexane besides regenerated stilbene.[2]

By contrast the *meso* diastereomer predominates in reactions of the red residues with diethyl sulfate. However, the extent of solvation seems to make little difference in the diastereomeric ratio, although the *meso* to *dd,ll* ratio is slightly higher (35% vs. 14%) from the solvate comprising 1 diadduct per 2 dioxahexane than the ratio (39% vs. 19%) from the 2 diadduct: 1 dioxahexane solvate. While this difference may not be highly significant, it may be

---

(1) B. M. Mikhailov and N. G. Chernova, *Doklady Akad. Nauk S.S.S.R.*, **74**, 939 (1950), *Chem. Abstr.*, **45**, 4698 (1951).

(2) A. G. Brook, H. L. Cohen, and G. F Wright, *J. Org. Chem.*, **18**, 447 (1953).

(3) J. W. B. Reesor and G. F Wright, *J. Org. Chem.*, **22**, 385 (1957).

noted that it corresponds with a greater regeneration of stilbene (41% *vs.* 33%) from the solvate yielding the lesser amount of *dd,ll* diastereomer. The correspondence indicates a steric effect, especially since the over-all yields of diastereomeric products are higher than was observed in the homogeneous alkylation.[2] Steric effects dependent on solvation have been suspected previously.[3]

It seemed to be of interest to examine the extent of solvation in the so-called stilbene-monosodium adduct,[4] but this examination proved to be impossible by the techniques which we employed. When a dioxahexane solution containing one molecule of stilbene per atom of sodium is evaporated at 25° its greenish brown color is displaced by a red color as the solution becomes more concentrated, until finally a red residue comprising equal amounts of diadduct and stilbene remains. When the residue is vacuum-evaporated at 100° and then is extracted with hexane to remove the stilbene the diadduct containing one half molecule of dioxahexane remains. Alkylation of the residue gives the same ratio (*ca.* 2.1) of diastereomeric 3,4-diphenylhexanes which were obtained from the authentic diadduct, which was prepared at 100°.

EXPERIMENTAL[5]

Azobenzene-dilithium adduct: 2,5-dioxahexane, 1:2. The solid-liquid 2-phase system from 1.82 g. (0.01 mole) of azobenzene and lithium in 40 ml. of dioxahexane after 72 hours of agitation was drained from the Schlenk tube to remove excess metal and then was evaporated for 4 hr. under nitrogen at 50° and 30 mm. Some of the yellow powder (0.3521 g.) was hydrolyzed with water. The organic portion was destroyed by boiling with nitric and sulfuric acid. The evaporated residue was ignited as lithium sulfate to redness and then weighed in absence of water: 0.1041 g., corresponding to a formula weight of 372 for the yellow powder.

A repetition in which the dioxahexane was removed at 100° under 1–5 mm. and the hydrolyzed residue was titrated with standard acid showed a formula weight of 376, identical with that calculated as 1 adduct plus 2 dioxahexane.

Another sample of yellow powder (0.01 mole) obtained after 100° at 30 mm. for four hours was hydrolyzed with 0.5 ml of water. The hydrolyzate was evaporated under 30 mm. at 50°–60° through a Drierite tower and then a trap chilled to −80°, the system finally having been flushed with nitrogen. In the trap was found 1.709 g. of dioxahexane, N_D^{20} 1.3799, b.p. 84° or 95% of that required for the 1:2 ratio specified above. The amount of dioxahexane obtained from the equivalent amount of red azobenzene-disodium adduct heated at 50° (30 mm.) was identical.

Finally a sample of the yellow powder which had been heated for 4 hr. at 100° (1 mm.) was treated with pure methyl sulfate in the manner described previously. A 75% yield of *N,N′*-dimethylhydrazobenzene, m.p. 33–34°, was obtained as well as a 20% yield of hydrazobenzene. Both products were characterized by mixture melting points.

N,N′-dibutylhydrazobenzene. A red solution prepared during 16 hr. from 1.82 g. (0.01 mole) of azobenzene, and a 5 mm.[3] piece of sodium in 40 ml. of dioxahexane was chilled to 0° and stored while 2.02 g. (0.022 mole) of 1-chlorobutane in 5 ml. of dioxahexane was added during 5 min. Then the green solution was warmed to 25° during 30 min., and was stirred while bleaching to orange, and finally a very light red color, occurred. The dioxahexane was vacuum-evaporated and the residue was dissolved in water and diethyl ether. The water-washed non-aqueous layer was evaporated and the residue was dissolved in 3 ml. of hexane. Chromatography by hexane elution through a 10 cm. × 1 cm. column of silicic acid (Mallinckrodt as received) yielded first the dibutylhydrazobenzene (m.p. 54–55°, 1.38 g.) in 40% yield. Two crystallizations from 4 ml. of absolute ethanol raised the m.p. to 57.2–57.7°.

Anal. Calcd. for $C_{20}H_{28}N_2$: C, 81.0; H, 9.53; N, 9.45. Found: C, 81.2; H, 9.90; N, 9.44.

Stilbene-disodium adduct: 2,5-dioxahexane, 1:2. A diadduct solution prepared from 0.9 g. (0.005 mole) of stilbene and an excess of sodium in 40 ml. of dioxahexane contained in a modified Schenk tube[4] was dropped during 3 hr. into a tared flask containing glass helices, which was maintained at 25° with a water bath and was continuously evacuated under 1 mm. This flask had been filled originally with nitrogen, and back-diffusion of air into it was prevented by introduction of a small amount of nitrogen into the exhaustion system.

After 0.71 g. of red residue had been collected in this manner it was treated with 50 ml of water-saturated diethyl ether. The water extract of the hydrolyzate was titrated with standard acid, showing that 75.2 mg. of sodium was present. The formula weight of 432 thus determined is 6% greater than that (406) of 1 stilbene-disodium adduct plus 2 moles of 2,5-dioxahexane.

Stilbene-disodium adduct: 2,5-dioxahexane, 2:1. (a) From the diadduct. A red residue prepared as described above was subsequently heated under vacuum at 100° for 40 min. Subsequent hydrolysis and titration showed that the formula weight of the residue was 285 or 5% greater than that (271) of 2 moles of stilbene-disodium adduct plus 1 mole of 2,5-dioxahexane.

(*b*) *From the monoadduct.* A brownish-green solution of stilbene-monosodium adduct prepared from 1.804 g. of stilbene and 0.23 g. of sodium in 40 ml. of dioxahexane was vacuum-evaporated at 100° as was described above. The light red residue was shaken with glass rods and commercial hexane (distilled into the system from sodium ketyl) until all of the solid was detached from the walls. The light red solution was decanted off. This extraction was repeated twice. The combined decantates (75 ml.) were washed with water. This aqueous extract contained 2.7% of the sodium originally introduced into the system. The non-aqueous layer upon evaporation yielded 0.895 g. (49.5%) of the stilbene originally introduced. This evidence that the diadduct was regenerated upon vacuum evaporation was confirned by the red solution found in dioxahexane from an aliquot of the hexane-insoluble residue. By contrast a portion of the residue before hexane extraction redissolved in dioxahexane to give a greenish-brown solution.

The formula weight of the hexane-extracted red residue was not determined. Isolation of dioxahexane after the red residue was bleached by carbon dioxide indicated a diadduct to dioxahexane ratio of 1:1 but this value must be questioned either because of the intractable behavior of the evaporating system or else because the metallic carboxylate may have retained dioxahexane of solvation.

3,4-Diphenylhexanes. Each of the diadducts from stilbene described above, in 0.005 mole quantity, was treated with an excess (5 ml.) of pure diethyl sulfate. After 4 hr. of agitation the disappearance of red color showed that reaction was complete. The system was extracted with commercial hexane and water containing 1 g. of sodium iodide for at least 3 min., in order to decompose excess ethyl sulfate. The hexane layer was evaporated to a small volume and then was chromatographed on a 30 cm. × 1 cm. column containing 150–170 mesh alumina (the narrow screen cut minimizes "coning")

---

[4] J. W. B. Reesor, J. G. Smith, and G. F Wright, *J. Org. Chem.*, 19, 940 (1954).

[5] Melting points have been corrected against reliable standards.

activated at 200° for one day. Elution with hexane yielded successively the *meso* diastereomer and then the *dd, ll,* isomer. Finally the column was eluted with methanol to remove stilbene. The yields for diadduct-dioxahexane, 1:2 were 0.33 g. (35%) *meso,* 0.13 g. (14%) *dd, ll,* characterized by the absorption peak at 280 mμ and 0.39 g. (41%) of stilbene characterized by mixture melting point. The yields from diadduct–dioxahexane 2:1 were 0.37 g. (39%) *meso,* 0.18 g. (19%) *dd, ll,* and 0.31 g. (33%) of stilbene. The *meso*-3,4-diphenylhexane was characterized by mixture melting point.[4]

A comparable experiment with diethyl sulfate and the red residue from the monoadduct after hexane extraction to remove stilbene yielded *meso* and *dd, ll*-3,4-diphenylhexane in a ratio of 2.1:1.

CHEMICAL LABORATORY
UNIVERSITY OF TORONTO
TORONTO 5, CANADA

2-Pyrones. XXVIII. 4,7,7-Trimethyl-7,8-dihydro-(2*H*,5*H*)-pyrano-[4,3-b]-pyran-2,5-dione

RICHARD H. WILEY, J. G. ESTERLE, K. F. HUSSUNG, C. L. DE SILVA, AND S. C. SLAYMAKER

Received May 20, 1957

On numerous occasions over the past several years we have observed the formation of a solid byproduct during the preparation of β-methylglutaconic anhydride. This solid, m.p. 154–155°, is best prepared by distillation of β-methylglutaconic acid at atmospheric pressure—a process that sometimes gives the anhydride and sometimes gives the byproduct. Its empirical composition, $C_{11}H_{12}O_4$, and molecular weight of 204 correspond to the combination of two molecules of β-methylglutaconic acid with the loss of one molecule of carbon dioxide. At various times we have considered several different structural possibilities for this material based on various types of condensations of two molecules of the anhydride. Of these only that of 4,7,7-trimethyl-7,8-dihydro-(2*H*,5*H*)-pyrano[4,3-b]pyran-2,5-dione[1] (I) is in accord with all of the physical and chemical data now available to characterize this product. We now have confirmatory evidence for this structure which establishes it with reasonable assurance.

Most structural possibilities, such as those based on Diels-Alder condensations, can be eliminated at once as the dimer shows no acidic, enolic, or ketonic properties and does not react readily with bromine. Although the dimer does not dissolve in cold alkali and cannot be saponified with aqueous or alcoholic alkali, it does react quantitatively with three moles of potassium hydroxide on refluxing in ethylene glycol to give a saponification equivalent of 69. Two moles of alkali are required by formula I for opening the rings and one for decarboxylation of the resultant isodehydroacetic acid analog. Phorone has been isolated as the product of this alkaline hydrolysis. Formation of phorone requires opening of both rings, decarboxylation at both carboxyl groups, and isomerization of the double bond. The carbon chain in the dimer is established by the isolation of this degradation product.

The spectral data for the dimer also confirm the structure I. Spectral analogies would be expected with the related open chain isopropyl isodehydroacetate (II). There is a remarkable parallel in the data for these two materials. The dimer absorbs in the ultraviolet at 254 mμ, log ϵ 3.984; 294 mμ, log ϵ 3.698. Isopropyl isodehydroacetate absorbs at 248 mμ, log ϵ 3.80; 295 mμ, log ϵ 3.78. The principal and characteristic infrared absorption bands occur at 1745 and 1718 cm.$^{-1}$ (2-pyrone and unsaturated delta lactone carbonyl stretching vibrations respectively); 1071 cm.$^{-1}$ (C=O stretching); and at 850 cm.$^{-1}$ (ethylenic C—H rocking vibration band characteristic of 2-pyrones). The related absorption bands for ethyl isodehydroacetate occur at 1754, 1727, 1080, and 850 cm.$^{-1}$ The dimer differs from the ethyl ester in having a relatively strong absorption band at 1406 cm.$^{-1}$, assignable to the C—H bending vibration of the conjugated methylene group. In both structures the 2-pyrone carbonyl absorption is shifted to higher frequencies, a phenomenon previously noticed with 2-pyrones having carbonyl substituents in the 5-position.[2]

The pyrolysis of the dimer is a most interesting reaction. The pyrolysis product, formed by heating the dimer to 350° in the presence of copper, is 4-methyl-6-(2′-methylpropenyl)-2-pyrone[3] (III) obtained by decarboxylative rearrangement of the acyl glutaconic anhydride obtained in turn from senecioyl chloride and β-methylglutaconic anhydride. The infrared absorption characteristics of the products obtained by the two processes are identical. The great diminution of the very strong band at 1080 cm.$^{-1}$, characteristic of the C—O stretching vibration in the unsaturated delta lactone structure of the dimer and one of the most prominent in its spectra, can be used to assess the purity of the 2-pyrone in which this band is very weak. It has been noted previously[4] that δ,δ-dimethyl-δ-valerolactone is converted to isoheptanoic acid at 216° in a similar reaction.

This conversion of β-methylglutaconic anhydride in two pyrolytic steps to 4-methyl-6-(2′-methylpropenyl)-2-pyrone has suggested the combination of these two steps into one as a more di-

---

[1] The product, ultimately identified as (I) will be referred to as the dimer in this discussion in the interests of brevity.

[2] Richard H. Wiley, and S. C. Slaymaker, *J. Am. Chem. Soc.*, **78**, 2393 (1956).

[3] Richard H. Wiley, and J. G. Esterle, *J. Org. Chem.*, **21**, 1335 (1956).

[4] R. P. Linstead and H. N. Rydon, *J. Chem. Soc.*, 580 (1933).