4,4'-diaminodibenzyl-2,2'-disulfonic acid (white pointed flat needles) which was found to be identical with an authentic sample prepared from the same starting material by reduction with tin and hydrochloric acid.[23]

Anal. Calcd. for $C_{14}H_{16}O_6N_2S_2$: N, 7.53. Found: N, 7.13. *Titration:* 99.03 mg. consumed 0.1 *N* sodium hydroxide 5.295 cc. Calcd. for $C_{14}H_{16}O_6N_2S_2$: 5.318 cc.

(b) From 4,4'-dinitrostilbene-2,2'-disulfonic acid (Note 4): 2 g. of 4,4'-dinitrostilbene-2,2'-disulfonic acid in 40 cc. of diethylene glycol with 8 cc. of hydrazine hydrate gave 0.8 g. (46.2%) of 4,4'-diaminodibenzyl-2,2'-disulfonic acid (white pointed flat needles).

Titration: 95.80 mg. consumed 0.1 *N* sodium hydroxide 5.12 cc. Calcd. for $C_{14}H_{16}O_6N_2S_2$: 5.14 cc.

4,4'-Diamino-α,β-diethyldibenzyl.—The reduction of 19.8 g. of *p*-nitropropylbenzene with 180 cc. of triethylene glycol, 30 g. of potassium hydroxide and 24 cc. of hydrazine hydrate gave 14 g. of dark oily product which was fractionally distilled.

Fraction I: 3.5 g. boiling at 86–87° at 4 mm., identical with *p*-aminopropylbenzene. It furnished an acetyl compound (plates), m. p. 95–96°.

Anal. Calcd. for $C_{11}H_{15}ON$: C, 74.53; H, 8.53; N, 7.90. Found: C, 74.68; H, 8.49; N, 8.03.

Fraction II: 5.1 g. boiling at 178–188° at 0.3 mm.; it solidified after standing. Recrystallization from a mixture of ether and petroleum ether (70–90°) and then from methanol gave about 2 g. of *meso*-4,4'-diamino-α,β-diethyldibenzyl (rhombic plates), m. p. 141–142°, not depressed by admixture with an authentic sample.[12]

The ether–petroleum ethereal mother liquor obtained above on concentration gave the racemic isomer in leaflets. Recrystallization from ether–petroleum ether gave 1.7 g., m. p. 97–98.5° (one sample recrystallized from methanol melting at 98–99°).

Anal. Calcd. for $C_{18}H_{24}N_2$: C, 80.54; H, 9.01; N, 10.43. Found: (*meso* form) C, 80.68; H, 9.12; N, 10.63; (racemic form) C, 80.50; H, 8.82; N, 10.71.

Both *meso* and racemic isomers furnished the dipropionyl compounds melting at 264–266° (plates) and 217–218° (plates), respectively, mixed with authentic samples[12] (*meso* form m. p. 262–264°; racemic form 207–215°[10]) melted at 263–266° and 210–216°, respectively.

4,4'-Dihydroxy-α,β-diethyldibenzyl.—0.14 g. of *meso*-diamino compound, m. p. 141–142°, was dissolved in dilute sulfuric acid and diazotized with sodium nitrite. After standing at 2–5° about twenty minutes and pouring in portions into 300 cc. of boiling water, the crystalline dihydroxy compound separated on cooling, m. p. 174–178° (0.12 g.). Recrystallization from benzene gave pure product, m. p. 181–182°, not depressed by admixture with an authentic sample of hexestrol.

Diazotization of racemic diamino compound (m. p. 97–98°) under the same conditions as above gave the racemic or isohexestrol which after repeated recrystallization from ether–petroleum ether melted at 128–129°, not depressed by admixture with an authentic sample.[12]

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found (*meso* form): C, 80.18; H, 8.14. (racemic form): C, 80.04; H, 8.22.

(23) Ris and Simon, *Ber.*, **30**, 2618 (1897).

Summary

1. The modified Wolf–Kishner method has been adapted for the reduction of aromatic nitroaldehydes.

2. Nitrotoluenes have been converted to the corresponding dimeric amino products and toluidines by using hydrazine hydrate.

3. Both the 4,4'-dinitrostilbenes and the 4,4'-dinitrodibenzyls have been converted to the diaminostilbenes or diaminodibenzyls by the action of hydrazine hydrate. In all of these cases the presence of alkali was a determining factor with respect to the formation of dimeric products and the persistence or the reduction of the ethylenic linkage.

4. A new synthetic route for the preparation of hexestrol has been described.

CAMBRIDGE 38, MASSACHUSETTS RECEIVED APRIL 17, 1948

[CONTRIBUTION FROM ROHM & HAAS COMPANY]

Preparation of Acetals or Ketals from Vinyl-type Esters

BY W. J. CROXALL, F. J. GLAVIS AND H. T. NEHER

In the course of an investigation of the addition of alcohols to vinyl compounds, it was observed that when vinyl acetate is added to an excess of alcohol containing a small amount of mercury oxide and boron trifluoride, heat is evolved and an acetal and acetic acid are formed in high yields. Under similar conditions isopropenyl acetate gives a ketal and acetic acid. The over-all course of the reaction is

$$CH_2{=}CHOCOCH_3 + 2ROH \longrightarrow CH_3CH(OR)_2 + CH_3COOH$$

Mixtures of mercuric oxide and the complexes formed from boron trifluoride with alcohols, ethers or carboxylic acids were found to be the most active catalysts. With these, the reaction starts promptly and is so rapid that efficient cooling is required to prevent vigorous or even violent boiling. Mercuric sulfate is a slightly less active catalyst. With mercuric phosphate no appreciable reaction occurs at room temperature, but after the mixture is refluxed for two hours, some hemiacetal acetate is formed. Coffman[1] obtained the 1-acetoxyethyl ether of a glycolic ester when equi-molar quantities of vinyl acetate and the glycolic ester were refluxed in the presence of mercuric phosphate. Mercuric oxide alone is entirely inert as a catalyst at room or elevated temperatures. Boron trifluoride diethyl etherate alone induces no exothermic reaction, but when the reaction mixture is refluxed, acetal is produced in low yield, together with acetic ester, acetaldehyde and water. Presumably, the initial reaction in this case is an alcoholysis[2] after which some of the acetaldehyde undergoes acetal formation

$$CH_2{=}CHOCOCH_3 + ROH \longrightarrow CH_3CHO + CH_3COOR$$
$$CH_3CHO + 2ROH \longrightarrow CH_3CH(OR)_2 + H_2O$$

(1) Coffman, U. S. Patent 2,384,726 (1945).

(2) Herrmann and Deutsch, British Patent 314,646 (1929).

The course of the reaction is believed to be quite different when the mercuric oxide boron trifluoride catalysts are used. No acetaldehyde could be detected when dry reagents were used. When the mole ratio of alcohol to vinyl acetate is less than two, 1-alkoxyethyl acetate occurs as one of the products. This compound is believed to be an intermediate in the reaction. It is suggested that the reaction proceeds as follows

(a) $CH_2{=}CHOCOCH_3 + ROH \longrightarrow CH_3CH(OR)OCOCH_3$

(b) $CH_3CH(OR)OCOCH_3 + ROH \longrightarrow CH_3CH(OR)_2 + CH_3COOH$

The plausibility of reaction (b) was clearly demonstrated when butyl acetal was obtained in 81% yield by the action of 1-butoxyethyl acetate on *n*-butyl alcohol in the presence of mercury oxide and boron trifluoride. The 1-butoxyethyl acetate was prepared from *n*-butyl vinyl ether and acetic acid.[3]

The reaction offers a convenient method for preparing acetals and is especially useful for preparing ketals. It is applicable to primary and secondary alcohols. Ethylene glycol forms the cyclic acetal, 2-methyl-1,3-dioxolane. Tertiary alcohols do not give the acetals but undergo alcoholysis to acetaldehyde and the tertiary alkyl acetates. Phenol undergoes a vigorous reaction with vinyl acetate under the reaction conditions to give acetic acid and alkali soluble polymeric materials. The yields of acetals from primary alcohols are 80–90% as compared to a 38% yield from isopropyl alcohol. The best yields are obtained when the reaction is carried out under anhydrous conditions. In one experiment in which 98% ethanol and undistilled vinyl acetate were used with mercuric sulfate as a catalyst, the yield of acetal was 58%, as compared to 88% when anhydrous reagents were used. Ethyl acetate was isolated in this experiment, indicating that some alcoholysis also occurred. The ketal yields are lower than the yields of the corresponding acetals. Table I lists some of the acetals and ketals prepared by this method.

TABLE I

ACETALS AND KETALS PREPARED

Acetals (of acetaldehyde)	B. p., °C. (mm.)	Yield, %	$n^{20}D$
Methyl	62.5–64	84	1.3665[a]
Ethyl	103–104	88	1.3809[a]
Isopropyl	126.5	38	1.3890[b]
n-Butyl	74.5–76(14)	89	1.4080[4]
Allyl	148–149.5	85	1.4218[c]
2-Methyl-1,3-dioxolane	82–83.5	68	1.3970[d]
Ketals (of acetone)			
Ethyl	113–113.5	55	1.3891[e]
n-Butyl	64–64.5(3)	63	1.4120[f]
Allyl	61–62(26)	32	1.4262[c]
2,2-Dimethyl-1,3-dioxolane	91–92	49	1.3980[g]

[a] "Beilstein," I, 671–672. [b] Adkins and Adams, THIS JOURNAL, **50**, 182 (1928). [c] Hurd and Pollack, *ibid.*, **60**, 1907 (1938). [d] Clarke, *J. Chem. Soc.*, **101**, 1804(1912). [e] Claisen, *Ber.*, **31**, 1012 (1898). [f] *Anal.* Calcd. for $C_{11}H_{24}O_2$: C, 70.16; H, 12.84. Found: C, 70.01; H, 12.79. [g] Otto, THIS JOURNAL, **59**, 1591 (1937).

The substitution of mercaptans for alcohols in the reaction gave 2-alkylmercaptoethyl acetates instead of mercaptals. The yield was about 75% when mercuric sulfate or mercuric oxide and boron trifluoride etherate was used, as compared to a 99% yield with boron trifluoride etherate alone as the catalyst. A 10% yield of the same product was obtained when the reaction mixture was refluxed without catalyst.

Experimental

Materials.—The alcohols were dried when necessary in the usual manner and carefully fractionated. The vinyl acetate was fractionated and material of b. p. 72.5–73° used. The isopropenyl acetate was obtained from Tennessee Eastman Corporation and material of b. p. 96° used. *n*-Butyl mercaptan was fractionated and material of b. p. 97° used.

Preparation of Acetals and Ketals.—The following preparation of *n*-butyl acetal is representative of the method used. In a one-liter three-necked flask equipped with a mercury-sealed stirrer, thermometer, dropping funnel and reflux condenser, were placed 148 g. (2.0 moles) of *n*-butyl alcohol, 1 g. of red mercuric oxide and 1 ml. of boron trifluoride diethyl etherate. To this was added 86 g. (1.0 mole) of vinyl acetate over a period of ten minutes while maintaining the temperature below 55° by means of an ice-bath. The mixture was allowed to stir for one hour, after which it was poured into a suspension of 56 g. (0.5 mole) of sodium carbonate in 250 ml. of water. The upper oil layer was separated and dried over anhydrous potassium carbonate. The aqueous layer was acidified with concd. hydrochloric acid, extracted with ether, dried over anhydrous sodium sulfate and distilled to give 26 g. of acetic acid, b. p. 116.5–117°, $n^{20}D$ 1.3721.

The oil layer upon distillation through a one-foot glass helices packed column gave 153 g. (88.5%) of *n*-butyl acetal, b. p. 74.5–76° (14 mm.), $n^{20}D$ 1.4080.[4]

When the mercuric oxide was omitted in the above experiment, a small amount (3 g.) of acetaldehyde, 18 g. of *n*-butyl acetate and 50 g. of butyl acetal was obtained. The major portion of the reaction mixture consisted of the starting materials and butyl acetate.

Reaction of *t*-Butyl Alcohol with Vinyl Acetate.—From 296 g. (4 moles) of *t*-butyl alcohol, 2 g. of mercuric oxide, 4 g. of methanol boron trifluoride complex (1:1) and 344 g. (4 moles) of vinyl acetate, there was obtained 5 g. of material trapped in a Dry Ice receiver (b. p. around 0°, decolorized a solution of bromine in carbon tetrachloride; thought to be isobutylene); 76 g., b. p. up to 97°; 69 g. (15%) *t*-butyl acetate, b. p. 97–98°, $n^{24}D$ 1.3875; 70 g. higher boiling material (98–170°), and considerable polymeric residue. Attempts to fractionate the 98–170° cut gave no constant boiling fractions.

Preparation of 1-(*n*-Butoxy)-ethyl Acetate from *n*-Butyl Vinyl Ether.—To 120 g. (2 moles) of acetic acid and one drop of concd. sulfuric acid was added with stirring 208 g. (2 moles) of *n*-butyl vinyl ether. The temperature during the addition was maintained below 45° by cooling. Stirring was continued for one and one-half hours and 0.5 g. of sodium methoxide was added. Distillation gave 265 g. (82.8%) of 1-(*n*-butoxy)-ethyl acetate, b. p. 65° (14 mm.), $n^{20}D$ 1.4025.[5] The saponification equivalent determined for this compound was 158, the calculated value is 160.

Preparation of *n*-Butyl Acetal from 1-(*n*-Butoxy)-ethyl Acetate.—Two moles of *n*-butyl alcohol (148 g.), 3 g. red mercuric oxide and 2 ml. of methanol boron trifluoride

(3) Reppe, "Advances in Acetylene Chemistry," 1940, trans. by R. F. C., Office of Rubber Reserve, July 25, 1945.

(4) Connor, Elving and Steingiser, *Ind. Eng. Chem.*, **40**, 498 (1948).

(5) Hurd and Green, THIS JOURNAL, **63**, 2202 (1941).

(1:1) were placed in a one-liter flask. To this was added with rapid stirring, 320 g. (2 moles) of 1-(*n*-butoxy)-ethyl acetate over a period of fifty-five minutes. The temperature was maintained at 10–20° by means of an ice-bath. Stirring was continued for thirty minutes, the reaction mixture poured into a suspension of 106 g. (1.0 mole) of sodium carbonate in 150 ml. of water, the oil layer separated, dried over anhydrous potassium carbonate and distilled to give 295 g. (85%) of *n*-butyl acetal, b. p. 185–189°, $n^{20}D$ 1.4080.[4]

Preparation of 2-Butylmercaptoethyl Acetate.—Upon mixing 90 g. (1 mole) of *n*-butyl mercaptan, 43 g. (0.5 mole) of vinyl acetate and 0.5 ml. of boron trifluoride etherate, the temperature rose slowly to 62°. The mixture was allowed to stand overnight and 1 g. of sodium methoxide added. Distillation gave 75 g. (99% yield based on vinyl acetate) of 2-butylmercaptoethyl acetate, b. p. 72–75° (2 mm.), $n^{20}D$ 1.4616.

With mercuric sulfate as the catalyst instead of boron trifluoride etherate, the yield of the mercapto-ester was 76%; with no catalyst present the yield of this ester amounted to only 10%.

Summary

1. Acetals are produced in good yield by the reaction of vinyl acetate with primary aliphatic alcohols in the presence of an acidic mercury catalyst.

2. Ketals are produced in a similar manner from isopropenyl acetate.

3. It is suggested that the vinyl acetate and alcohol initially react to form a hemiacetal acetate, which subsequently reacts with alcohol to give an acetal and acetic acid.

PHILADELPHIA, PA. RECEIVED APRIL 1, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Some Diethylisopropoxyhalogenosilanes and their Hydrolysis Products[1]

BY PATRICK A. MCCUSKER AND CHARLES E. GREENE

Although a number of alkoxyfluorosilanes and some alkylalkoxychlorosilanes have been prepared, no alkylalkoxyfluorosilanes have been previously reported. In the course of the preparation of a compound of this type, some previously unreported organosilicon compounds were prepared and some observations made on the hydrolysis of diethylisopropoxyhalogenosilanes.[2]

Direct reaction of excess isopropyl alcohol and diethyldichlorosilane gave yields of only 20% of diethyldiisopropoxysilane while yields of 67% have been reported for the analogous preparation of dimethyldi-*n*-butoxysilane.[3] The lower yield of the isopropoxy compound may be attributed to the greater steric requirements of the isopropoxy group or to the general lower reactivity of the secondary alcohol compared to the primary. A low yield of diethylisopropoxyfluorosilane (22%) was obtained from the reaction of zinc fluoride on diethylisopropoxychlorosilane. This is probably due to a competing reaction in which both the alkoxy and chloro substituents are replaced by fluorine.

An aqueous suspension or a homogeneous solution of 0.04 molar diethylisopropoxyfluorosilane in a methanol–water mixture, maintained a hydrogen ion concentration of less than 10^{-4} mole per liter, as indicated by the basic color given by methyl orange which is unchanged on standing several days. Using phenolphthalein as an indicator, however, the suspension in water could be rapidly titrated to a stoichiometric end-point with 0.1 *N* base. A calculation of the concentration of hydrogen fluoride necessary to produce a hydrogen ion concentration of 10^{-4} mole per liter indicated that the hydrolysis came to equilibrium when less than 0.3% of the fluoride has been hydrolyzed in neutral water. At a somewhat lower hydrogen ion concentration, 10^{-10} mole per liter, hydrolysis proceeded to completion very rapidly.

On the hydrolysis of diethylisopropoxychlorosilane, with an equivalent amount of base, even in the presence of excess isopropyl alcohol, the alkoxy group split off and the cyclic trimer and tetramer were formed in high yield. [Diethyldiisopropoxysilane was found, however, to be stable in excess base.] Justification for the assignment of formulas to the two cyclic compounds is based on the analytical composition, molar refraction and molecular weight determination. The absence of any hydroxyl groups was further shown by the application of the Zerewitinoff reaction.

A marked difference in the action of sodium on the cyclic trimer and the cyclic tetramer was incidentally observed. The trimer on heating with sodium in the temperature range 150 to 245° evidently underwent a polymerization resulting in a marked increase in viscosity. The tetramer, on the other hand, was completely unaffected by long heating with finely divided sodium at 295°.

Experimental

The reaction apparatus used in this work consisted of a 1-liter, 3-necked flask equipped with stirrer and reflux condenser and protected from atmospheric moisture. All products were purified by fractional distillation through a total reflux, partial take-off column, 12 mm. inside diameter and 53" in height, packed with 1/8" glass helices. The column was operated at a reflux ratio of ten to one. Carbon and hydrogen analyses were made by Micro-Tech Laboratories, Skokie, Illinois, and hydrolyzable halogen was determined by titration of aqueous mixtures with standard base. Molar refractions were calculated from the bond refraction values of Warrick[4] and molecular

(1) This paper consists of a report of work done under contract with the Technical Command, Chemical Corps, U. S. Army.

(2) The authors wish to thank Dr. Charles C. Price for his helpful interest in this work.

(3) Sauer, THIS JOURNAL, **68**, 138 (1946).

(4) Warrick, *ibid.*, **68**, 2455 (1946).