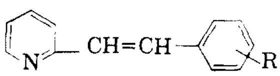
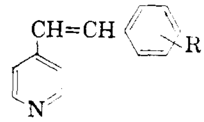
TABLE II[a]

2(AND 4)-STILBAZOLES OBTAINED BY THE CONDENSATION OF AROMATIC ALDEHYDES WITH 2(AND 4)-PICOLINE IN ACETIC ANHYDRIDE (METHOD B)

Compound	R	Yield, %	M.p. or B.p., °C.	Mm.	Formula	Carbon Calc'd	Carbon Found	Hydrogen Calc'd	Hydrogen Found	Nitrogen Calc'd	Nitrogen Found
						2-Stilbazoles					
XIV	H	52	91–92[b]		$C_{13}H_{11}N$	86.17	86.17	6.12	6.07	7.73	7.78
			140–142	2.5							
XV	*3,4*-CH_2O_2	61	111–112		$C_{14}H_{11}NO_2$	74.66	74.51	4.92	4.82	6.22	6.20
			180–181	2							
XVI	*o*-NO_2	57	102–103[c]		$C_{13}H_{10}N_2O_2$	69.17	69.10	4.45	4.42	12.39	12.34
XVII	*m*-NO_2	94	131–132[d]		$C_{13}H_{10}N_2O_2$	69.17	69.01	4.45	4.39	12.39	12.24
XVIII	*p*-NO_2	91	140–141[e]		$C_{13}H_{10}N_2O_2$	69.17	69.05	4.45	4.36	12.39	12.74
XIX	*o*-Cl	57	76–77		$C_{13}H_{10}ClN$	72.38	72.29	4.67	4.57	6.49	6.28
			108–110	2							
XX	*p*-CH_3COO	76	114–115		$C_{15}H_{13}NO_2$	75.28	75.27	5.47	5.60	5.85	5.69
XXI	*o*-CH_3COO	58	180–181	3.5	$C_{15}H_{13}NO_2$	75.28	75.45	5.47	5.48	5.85	5.98
						4-Stilbazoles					
XXII	H	92	129–130[f]		$C_{13}H_{11}N$	86.17	86.00	6.12	5.99	7.73	7.57
XXIII	*m*-NO_2	97	144–145[g]		$C_{13}H_{10}N_2O_2$	69.17	69.05	4.45	4.49	12.39	12.61
XXIVA[h]	*o*-CH_3COO	74	118–119		$C_{15}H_{13}NO_2$	75.28	75.44	5.47	5.51	5.85	5.76
B	*o*-CH_3COO	67	197–198		$C_{15}H_{13}NO_2$	75.28	75.35	5.47	5.81	5.85	6.10
XXV	*p*-CH_3COO	68	167–168		$C_{15}H_{13}NO_2$	75.28	75.19	5.47	5.37	5.85	5.67
XXVI[i]	*p*-OH	90	264–265[j]		$C_{13}H_{11}NO$	78.77	78.47	5.60	5.79	7.07	6.87

[a] Solvent of recrystallization was methanol for XVII, XVIII, XXIII, and XXVI; isopropyl alcohol for XXII; low-boiling petroleum ether for XVI, XX, XXIVA; 1,4-dioxane for XXIVB; and acetonitrile for XXV. [b] Blout *et al.* [*J. Am. Chem. Soc.*, **67,** 1315 (1945)] reports m.p. 89°. [c] Reference 2 reports m.p. 101° for the *trans* isomer. [d] Feist [*Ber.*, **34,** 465 (1901)] reports m.p. 127°. [e] Reference *d* reports m.p. 125–126°. [f] Reference *b* reports m.p. 130°. [g] Friedländer [*Ber.*, **38,** 2838 (1905)] reports m.p. 138°. [h] Ultraviolet spectra: XXIVA, λ 298 mμ; ε 26,580; XXIVB, λ 287, 332 mμ; ε 21,140, 19,220. [i] Obtained by 72-hour refluxing. [j] Chiang and Hartung [*J. Org. Chem.*, **10,** 21 (1945)] reports m.p. 215–217°.

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The Acetylation of Organic Hydroxy Compounds with Ketene

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The use of ketene in acetylating glycols, Cellosolves, carbohydrates, and other polyhydroxy organic compounds appears to be rather limited. Van Alphen[2] reports an unsuccessful attempt to acetylate glucose with ketene, while Hurd[3] and his associates, using acetone, dioxane, and pyridine as solvents and a trace of sulfuric acid as catalyst, obtained syrups which defied purification. Gwynn and Degering[4] report that ketene reacts with acetone and pyridine and this fact may have been a serious complication in the final purification. In addition Rice and Greenburg[5] have studied the rate of polymerization of ketene in various solvents and found this tendency to be a serious complication in many instances. Acetone was a rather serious offender in this regard. However, the rate of polymerization of ketene in carbon tetrachloride was the lowest of the twenty different solvents tested. The reaction constant calculated according to the bimolecular law was 0.0000465 for carbon tetrachloride and 0.0146 for acetone, both at 0°. This means that at 0° ketene polymerizes approximately 300 times faster in acetone than in carbon tetrachloride. This may offer a plausible explanation for the greater difficulty encountered in purifying the acetylation product when acetone was used as solvent.

Significant contributions to carbohydrate and other hydroxy compound acetylations with ketene

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[2] J. Van Alphen, *Rec. trav. chim*, **43,** 823 (1924).

[3] C. D. Hurd, S. M. Cantor, and A. S. Roe, *J. Am. Chem. Soc.*, **61,** 426 (1939).

[4] B. H. Gwynn and E. F. Degering, *J. Am. Chem. Soc.*, **64,** 2216 (1942).

[5] F. O. Rice and J. Greenburg, *J. Am. Chem. Soc.*, **56,** 2132 (1934).

have been made by several other investigators.[6–9] Ketene has now been used to acetylate ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, Methyl Cellosolve,[10] Cellosolve,[10] Butyl Cellosolve,[10] glycerol, sorbitol, mannitol, and D-glucose. For this particular study ketene was prepared by the pyrolysis of acetone using a modified ketene lamp[11] and all acetylations were conducted in a type of absorption apparatus previously described.[12] Carbon tetrachloride, not previously reported, has been found to be a suitable solvent for acetylating the solid polyhydroxy compounds. The two hydroxy groups in each of the glycols were acetylated and glycerol produced the triacetate. The ether linkage in diethylene glycol, triethylene glycol, and the several Cellosolves was not ruptured by ketene under the experimental conditions used, even though the Cellosolves were each in turn treated with twice the theoretical amount of ketene.

EXPERIMENTAL

Acetylation of liquid hydroxy compounds. Weighed quantities, 30 to 50 g., respectively of ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, glycerol, Methyl Cellosolve, Cellosolve, and Butyl Cellosolve, were each acetylated in turn at room temperature by placing the weighed sample in the absorption apparatus[12] together with one or two drops of 18 *molar* sulfuric acid. Ketene then was passed into the apparatus for a period of time slightly in excess of that theoretically required to acetylate the hydroxy groups known to be present in the compound. The several acetates were purified by treatment with anhydrous sodium carbonate and vacuum distillation. The results are summarized in Table I.

Acetylation of solid hydroxy compounds. After studying the solvent effect of numerous organic compounds, carbon tetrachloride was found to be a suitable solvent for the acetylation of sorbitol, mannitol, and D-glucose. The final technique developed was to saturate the solvent with 18 *molar* sulfuric acid. A suspension of 5 g. of solid hydroxy compound in 40 ml. of prepared solvent was placed in the absorption apparatus.[12] A micro-burner was placed under the absorption apparatus and enough heat was supplied to keep the solvent refluxing gently. Ketene then was passed through the solution as long as absorption took place. The completion of the reaction was easily detected since the acetylation product was completely soluble in the hot carbon tetrachloride, whereas the initial hydroxy compound was only slightly soluble.

After acetylation the carbon tetrachloride solution was shaken with dilute sodium carbonate solution to neutralize the acid catalyst and any acid substances formed during acetylation. The carbon tetrachloride solution then was washed twice with water and the solvent was removed by distillation on a steam-bath. This treatment left a brown oily residue to which water was added and the last traces of carbon tetrachloride were removed by boiling. A sufficient quantity of ethanol then was added to dissolve the product when the solution was hot, and the solution was decolorized with Norit, filtered hot, and allowed to crystallize. If necessary the product was recrystallized from water-ethanol with a second Norit treatment. This treatment yielded sharp-melting products which then were dried in a vacuum desiccator. The products were characterized by their melting points, combustion analysis, and acetyl values. The results are again summarized in Table I.

No difficulty was encountered in obtaining a crystalline product from the acetylation of D-glucose in carbon tetrachloride. However, Hurd[3] reports that he obtained a syrup which defied all crystallization attempts when he acetylated D-glucose in acetone solution. His procedure was repeated and a similar syrup was obtained. However, on standing for several days, long crystals appeared in the syrup. Varying the procedure somewhat, the acetone was distilled off and the product was dissolved in carbon tetrachloride. The resulting solution was washed with a large quantity of sodium carbonate solution, then twice with water, and the solvent was distilled off on a steam-bath. The brown syrup remaining was recrystallized five times from a water-ethanol solution before a sharp-melting product was obtained.

The saponification equivalents were determined by standard published methods.[13] A modified procedure was developed for the semi-micro determination of acetyl groups, the fundamental principle of which was to hydrolyze the ester, and then to distill the acid quantitatively into a known amount of standard alkali. A weighed sample (0.2–0.4 g.) of the acetate was gently refluxed in a 50-ml. Claisen flask with 5 ml. of approximately 6 *molar* sulfuric acid for 1 hour. The contents of the flask were cooled and partially neutralized with 5 ml. of 6 *N* sodium hydroxide solution. The apparatus then was arranged for a traditional vacuum distillation so that the distillate was collected under the surface of a known amount of standard sodium hydroxide solution. Water was repeatedly added to the hydrolysis mixture to compensate for distillation loss until all volatile acetic acid was distilled. At this point 10 ml. of saturated barium hydroxide solution was added to the distillate to precipitate any sulfuric acid present, and the excess alkali was titrated with standard acid, allowance being made for the added barium hydroxide. The acetyl values, in general, were consistently high. This may be due to the reduction of some sulfuric acid during the initial hydrolysis of the acetate, and subsequent distillation of the more volatile reduction products. Blank runs were made in some cases, using an amount of the original hydroxy compound equivalent to the acetate taken in the determination. When this correction for the blank determination was subtracted from the original values, more satisfactory results were obtained, as shown in the case of sorbitol pentaacetate.

DISCUSSION

The selection of a suitable solvent is evidently of major importance in acetylating solid polyhydroxy compounds with ketene. Such a solvent should not react with ketene to form objectionable by-products, but should have suitable solvent character-

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[6] C. S. Vestling and M. C. Rebstock, *J. Biol. Chem.*, **152**, 585 (1944).

[7] G. H. Morey, *Ind. Eng. Chem.*, **31**, 1129 (1939).

[8] C. A. Burkhard and E. F. Degering, *Rayon Textile Monthly*, **23**, 340 (1942).

[9] E. A. Talley and L. T. Smith, *J. Org. Chem.*, **10**, 101 (1945).

[10] "Methyl Cellosolve, Cellosolve, and Butyl Cellosolve" are trade names of Carbide and Carbon Chemicals Corp. "Cellosolve" is 2-ethoxyethanol; "Methyl Cellosolve" is 2-methoxyethanol; "Butyl Cellosolve" is 2-butoxyethanol.

[11] R. E. Dunbar and L. L. Bolstad, *J. Org. Chem.*, **9**, 219 (1944).

[12] L. L. Bolstad and R. E. Dunbar, *Ind. Eng. Chem., Anal. Ed.*, **15**, 498 (1943).

[13] Shriner and Fuson, *The Systematic Identification of Organic Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 134.

TABLE I

PHYSICAL CONSTANTS OF ORGANIC ACETATES

Organic Hydroxy Compounds Acetylated	Acetyl Groups Introduced	Boiling Point, 0°/mm.		Density 20/4		Index of Refraction	Molecular Refraction		Sapon. Equiv.		Acetyl, %		Analysis C		Analysis H	
		Lit.	Obsv'd.	Lit.	Obsv'd.		Theor.	Calc'd	Theor.	Obsv'd.	Theor.	Obsv'd.	Calc'd	Found	Calc'd	Found
Ethylene glycol	2	188–190[a]	88–89/5 185.6/733	1.108[a] (14/4)	1.1053	1.4146	33.22	33.08	73.1	70.9	—	—	49.31	49.18	6.90	6.85
Propylene glycol	2	188/758[a]	182/739	—	1.0547	1.4121	37.83	37.69	80.1	79.58	—	—	52.49	52.26	7.55	7.51
Diethylene glycol	2	245–251[b]	199/732	—	1.1144	1.4285	44.10	43.95	95.1	94.9	—	—	50.52	50.37	7.42	7.38
Triethylene glycol	2	300[b]	275.6/740	—	1.1172	1.4368	54.97	54.91	117.12	117.2	—	—	51.27	50.87	7.74	7.66
Glycerol	3	258–259[a]	256/720	1.160	1.1596	1.4298	48.72	48.59	72.37	72.37	—	—	49.54	49.41	6.46	6.38
Methyl Cellosolve	1	144.5/762[b]	141/732	1.0090[b] (14/14)	1.0062	1.4011	28.59	28.53	—	—	36.43	41.11	50.83	50.96	8.53	8.73
Cellosolve	1	158[b]	152–153/733	—	0.9751	1.4038	33.21	33.12	132.16	129.3	—	—	54.53	54.28	9.21	9.11
Butyl Cellosolve	1	—	185.5/740	—	.9425	1.4121	42.44	42.29	—	—	26.88	29.04	59.97	60.13	10.06	10.32
		Melting Point														
Mannitol	6	123–124[c]	123–124	—	—	—	—	—	—	—	59.42	61.73	49.76	50.06	6.03	5.97
Sorbitol	6	95[d]	98–99	—	—	—	—	—	—	—	59.42	59.36	49.76	49.62	6.03	6.14
D-Glucose (in CCl_4)	5	112–113[a]	112	—	—	—	—	—	—	—	52.56	56.85	49.20	49.42	5.64	5.87
D-Glucose (in Acetone)	5	112–113[a]	111–112	—	—	—	—	—	—	—	52.56	55.53	49.20	49.66	5.64	5.81

[a] Lange, *Handbook of Chemistry*, Fourth Ed., Handbook Publishing Co., Sandusky, Ohio (1941). [b] Beilstein's *Handbuch der Organischen Chemie*, Vierte Auflage. [c] R. M. Man- and C. S. Hudson, *J. Am. Chem. Soc.*, **64**, 926 (1942). [d] E. Pacsu and F. V. Rich, *J. Am. Chem. Soc.*, **55**, 3022 (1933).

istics for the polyol and its acetylated derivative. Solvents given preliminary attention were chloroform, carbon tetrachloride, ether, dioxane, ethyl acetate, acetic acid, benzene, and absolute ethanol. Of these carbon tetrachloride appeared to be most satisfactory.

Acetylation of D-glucose in carbon tetrachloride was found to be superior to acetylation in acetone in several respects. In the first place fewer steps are involved in the isolation of the final product. Secondly, a purer product is formed. Evidently the acetone solution is compatible with undesirable acidic side reactions as is indicated by the greater amount of sodium carbonate required in washing. The work of Rice and Greenburg[5] further substantiates this conclusion.

All available hydroxy groups in four typical glycols, glycerol, three Cellosolves, D-glucose, sorbitol, and mannitol were completely acetylated with ketene in the presence of a trace of sulfuric acid. Available ether linkages were not ruptured under similar treatment. Carbon tetrachloride was found to be a suitable solvent for the acetylation of solid polyols and definitely superior to acetone.

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The Addition of Trichlorosilane to Pentene-1 with Peroxide Initiators

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The addition of organosilicon hydrides and tribromosilane to olefinic double bonds in the presence of peroxide initiators has recently been described.[1] In continuing this work, using trichlorosilane, certain factors influencing the addition were observed.

The addition proceeds by a free radical mechanism, very likely as it is described by Sommer, *et al.*[2]

$$A\cdot + HSi\equiv \longrightarrow AH + \cdot Si\equiv$$
$$RCH{=}CH_2 + \cdot Si\equiv \longrightarrow R\underset{\cdot}{C}HCH_2Si\equiv$$
$$R\underset{\cdot}{C}HCH_2Si + HSi\equiv \longrightarrow RCH_2CH_2Si\equiv + \cdot Si\equiv$$

In this mechanism A· is the free radical initiating the chain reaction. The manner in which the chain terminates is not known.

Burkhard and Krieble[3] have pointed out that mixtures containing methyldichlorosilane gave relatively poor yields of adduct per mole of initiator (peroxide efficiency). Trichlorosilane gave much better results and peroxide efficiencies as high as 17 were obtained with pentene-1 with diacetyl peroxide. We have found that this value may under favorable conditions rise considerably, for example, reaching 300 (Table III).

In order to find some of the factors influencing yields and peroxide efficiencies, a series of experiments were carried out in which pentene-1, trichlorosilane, and *tert*-butyl perbenzoate were mixed and sealed into small Claisen flasks. After a period of heating, the flasks were opened and the contents were distilled from them. Very good material balances and a fairly accurate estimate of yields were obtained in this way. To these flasks were also added miscellaneous components thought likely to have an effect on the yields. Such materials as silicone stopcock grease, traces of water, alcohol, nickel, lead, zinc, air, nitrogen, or carbon dioxide had little or no effect. Certain other materials had very obvious effects. Table I summarizes some results obtained in this way.

Metals and their salts may either hinder or aid the reaction. Iron and its salts were outstanding in preventing the formation of adduct. Tin was a promoter for the reaction, causing successful addition, at temperatures lower than those normally effective. Tin and its salts showed no catalytic activity alone, however, but presumably through some action on the peroxide acted as an effective promoter. Tin mixed with stannic chloride caused the addition to become violent even at room temperature.

Three samples of tin were tested and found to possess greatly differing effects as promoters. Granular tin (No. 1) used in Table II was 20 mesh, lot 15, from Baker and Adamson Co. A sample (No. 2) from J. T. Baker Co., 20 mesh, reagent grade, lot 3787, was less effective. A third sample (No. 3) filed from a bar of commercial tin of uncertain origin proved to be far the best. Addition of small amounts of it to the mixtures at room temperature caused violent reactions. Each sample of tin was analyzed spectroscopically and showed increasing activity with increasing amounts of impurities although the trace elements responsible could not be identified.

Experiments using various initiators showed appreciable differences as might be expected. Benzoyl peroxide was very active and gave high peroxide efficiencies, but in certain mixtures tended to react so rapidly as to make control difficult. Table III summarizes some data concerning initiators and the effects of temperature. Higher temperatures than employed here would be likely to improve the yields from some of the initiators.

The pentyltrichlorosilane obtained as the product from all these experiments was examined closely to establish its identity beyond question. Sommer[2] has found that octene-1 and trichlorosilane formed *n*-

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(1) J. L. Speier, Ruth Zimmerman, and J. A. Webster, *J. Am. Chem. Soc.*, **78**, 2278 (1956).

(2) L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *J. Am. Chem. Soc.*, **69**, 188 (1947).

(3) C. A. Burkhard and R. H. Krieble, *J. Am. Chem. Soc.*, **69**, 2687 (1947).