1-(*p*-Bromophenyl)-3-phenyl-5-(*p*-chlorophenyl)-pyrazoline.—The theoretical amount of 4-bromophenylhydrazine in acetic acid was added to a warm solution of *p*-chlorobenzylidene-acetophenone. The crystals that separated during the first few hours turned out to be *p*-bromophenylhydrazine. The filtrate, which was nearly black by reflected light, gave a 31% yield of pyrazoline on standing for twenty-four hours longer. Fine, cream-colored crystals were obtained by crystallization from alcohol; m. p. 142–143°. The product was not affected by boiling acetic acid or by sodium amalgam, which indicated that it was not a hydrazone.

Anal. Subs., 0.4104: 19.85 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{21}H_{16}N_2ClBr$: halogen, 28.06. Found: 27.90.

Summary

1. A method has been described for the preparation of methyl-3-bromo-4-acetylaminophenyl ketone and its structure has been established.
2. A condensation product from phenylhydrazine and benzalacetophenone different from that reported by Auwers and Voss has been obtained. Its behavior toward sodium amalgam and its rearrangement when heated with acetic acid show that it is a hydrazone.
3. A number of new halogen substitution products of 1,3,5-triphenylpyrazoline have been obtained. In the preparation of these compounds we have been unable, thus far, to confirm Straus' conclusion that the presence of halogen substituents in all three of the phenyl radicals of the hydrazone of benzalacetophenone stabilizes the compound. Further study is in progress in which it is hoped to test the effect of molecular symmetry of the ketone in this rearrangement.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE EFFECT OF CERTAIN BETA SUBSTITUENTS IN THE ALCOHOL UPON AFFINITY AND REACTIVITY IN ACETAL FORMATION

BY JOHN N. STREET AND HOMER ADKINS

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The study of the relations of the structure of the alcohol and aldehyde to the affinity and reactivity manifested in acetal formation has been continued by determining the location of the equilibrium point of the reaction of acetaldehyde with various alcohols which may be regarded as β substitution products of ethanol. The type reaction may be represented as follows

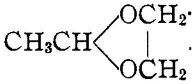
$$CH_3CHO + 2RCH_2CH_2OH \rightleftharpoons CH_3CH(OCH_2CH_2R)_2 + H_2O$$

The β substituents used were the chloro, bromo, iodo, ethoxy, methoxy, methylene, carbethoxy, amine hydrochloride and nitro groups.

The methods of experimentation and the concentrations of reactants were essentially the same as those previously described.[1,2] The equilibrium points were determined from both sides in the case of the three halohydrins, phenylethanol and methoxy- and ethoxy-ethanols.

The Seyewetz-Bardin sulfite method was in most cases used for the determination of acetaldehyde. The hydrogen peroxide method was used in some instances. It was necessary to introduce a correction factor in the case of the halohydrins which hydrolyzed slowly during the titration.

In the case of amino-ethanol, acetal formation cannot take place in the usual way as the amino group reacts with the aldehyde. The acetal reaction must consequently be carried out with a salt of the amine. The hydrochloride is insoluble in most organic solvents so that the reaction must be allowed to occur in a water solution. The solution of the amine in water was made slightly acid with hydrogen chloride, the aldehyde added at 0° and the reaction allowed to proceed at room temperatures for a week. A sample of the reaction mixture was rendered just alkaline to phenolphthalein and then added to a sulfite solution and titrated in the usual way. The end-point is not clear. The hydrogen peroxide method was also used for the determination of the aldehyde. The results obtained were in good agreement with those obtained by the sulfite method. The reaction of ethanol and acetaldehyde was run under conditions similar to those used for amino-ethanol. The equilibrium constant found was 0.0618 instead of 0.0744 as found using 1 mole of alcohol and 0.091 mole of aldehyde.

An attempt was made to prepare β,β′-hydroxydiethylacetal, $CH_3CH(OCH_2CH_2OH)_2$, by the reaction of acetaldehyde and ethylene glycol. However, even when two moles of the glycol were used with one mole of acetaldehyde, there was a good yield of ethylene acetal  $CH_3CH\left\langle\begin{matrix}OCH_2\\ |\\ OCH_2\end{matrix}\right.$.

Attempts to use the sulfite, the hydrogen peroxide and the Hartung colorimetric method were alike unsuccessful in determining acetaldehyde or water in the presence of nitro-ethanol. The amount of acetal that could be isolated from a reaction mixture of two moles of nitro-ethanol and one of acetaldehyde was determined and the equilibrium constant calculated from this. A mixture of 1 mole of nitro-ethanol and 0.091 mole of acetaldehyde was made and allowed to stand for two weeks. A sample of the reaction mixture was poured into a solution of sodium ethoxide to prevent further acetal formation or hydrolysis. The aldehyde present was then removed by distillation, collected and titrated. An equilibrium constant was calculated on the basis of the amount found. This value (0.0403) was too high because it was impracticable to collect all of

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[1] Adkins and Adams, This Journal, 47, 1368 (1925).

[2] Hartung and Adkins, *ibid.*, **49**, 2517 (1927).

the aldehyde. The value calculated from the amount of nitro-ethyl acetal isolated (0.0119) was too low because of losses of the acetal. The true value lies between these limits.

The methods used in the preparation of the reagents and their boiling points are given in Table I and the footnotes. Five acetals not hitherto prepared were obtained using the standard methods of preparation. The boiling points and the analytical data for these compounds are given in Table II.

TABLE I

THE METHODS OF PREPARATION AND PURITY OF REAGENTS

Compound	Boiling point
Ethylene chlorohydrin[a]	43° (3–4 mm.)
Ethylene bromohydrin[b]	56–57° (20 mm.)
Ethylene iodohydrin[c]	86–87° (25 mm.)
β-Ethoxy-ethanol[d]	134° (740 mm.)
β-Methoxy-ethanol[d]	124° (740 mm.)
β-Phenylethanol[e]	99–100° (10 mm.)
Ethyl hydracrylate[f]	94–95° (22 mm.)
β-Amino-ethanol	121° (740 mm.)
β-Nitro-ethanol[g]	......
Propanol	96.0–96.1° (740 mm.)
Acetaldehyde[h]	21–22° (740 mm.)

[a] Commercial ethylene chlorohydrin was dried for several days over anhydrous potassium carbonate and distilled under a pressure of 3–4 mm. at 43°. The samples used for reaction with aldehyde gave no precipitate with a 10% solution of silver nitrate, no color with copper sulfate and only a trace of acidity.

[b] Read and Williams, *J. Chem. Soc.*, **111**, 240 (1917); Read and Hook, *ibid.*, **117**, 121 (1920).

[c] Henry, *Bull. acad. roy. Belg.*, [3] **28**, 182 (1889); Wieland and Sakellarios, *Ber.*, **53B**, 201 (1920). It was found advantageous to cut the time of refluxing from 24 to 4 hours, a yield of 85–90% being obtained.

[d] Cretcher and Pittenger, THIS JOURNAL, **46**, 1505 (1924).

[e] β-Phenylethanol from a commercial source was kept over solid oxalic acid for several days and then distilled. Later it was dried over lime and again distilled.

[f] Drushel and Holden, *Am. J. Sci.*, **40**, 511 (1915). Drushel and Holden report that the ester prepared from β-iodopropionic acid has a b. p. at 22 mm. of 95.5°. The hydracrylic acid was prepared by the hydrolysis of ethylene cyanohydrin. [Erlenmeyer, *Ann.*, **191**, 268 (1878).] After filtering off the ammonium chloride, the solution was neutralized with sodium hydroxide, evaporated to dryness and the sodium hydracrylate extracted with absolute alcohol. The salt was recrystallized once from alcohol, dissolved in alcohol and enough of an alcoholic solution of hydrogen chloride added to precipitate 90% of the sodium. The esterification was then carried out using copper sulfate (free of sulfur trioxide) as a catalyst.

[g] Wieland and Sakellarios, *Ber.*, **53B**, 201 (1920).

[h] Child and Adkins, THIS JOURNAL, **45**, 3013 (1923).

A summary of the equilibrium constants and calculated values for —$RT \ln K$ is given in Table III. The compounds have been arranged in order of decreasing affinity as measured by decreasing equilibrium con-

TABLE II

BOILING POINTS AND ANALYTICAL DATA FOR CERTAIN ACETALS

Acetal of	B. p.	Analyses Calcd., %	Analyses Found, %
Ethylene chlorohydrin	109–110° (30 mm.)	Cl 37.93	37.95
Ethylene bromohydrin	129–130° (20 mm.)	Br 57.92	58.07
β-Methoxy-ethanol	100° (20–30 mm.)	C 53.84	53.80
		H 10.18	10.03
β-Ethoxy-ethanol	83–85° (10–15 mm.)	C 58.20	58.06
		H 10.75	10.78
β-Phenylethanol	201° (15 mm.)	C 79.94	80.16
		H 8.20	8.27

TABLE III

THE EFFECT OF CERTAIN SUBSTITUENTS IN THE ALCOHOL UPON AFFINITY IN ACETAL FORMATION

Alcohol	β Subs.	Vol., cc.	Conv. to acetal, %	K	$-RT \ln K$
β-Amino-ethanol	$HCl\cdot NH_2$	...	[a]	0.235	960 ± 100
n-Butanol	C_2H_5	97.1	95.8[b]	.1850	994 ± 50
Phenylethanol	C_6H_5	124.2	87.55[b]	.0978	1372 ± 50
Ethylene iodohydrin	I	83.3	90.50[b]	.0953	1387 ± 50
β-Ethoxy-ethanol	C_2H_5O	101.8	88.92[b]	.0939	1396 ± 50
n-Propanol	CH_3	79.7	90.50[b]	.0902	1420 ± 50
β-Methoxy-ethanol	CH_3O	83.9	88.63[b]	.0754	1525 ± 50
Ethanol	H	63.0	90.94[b]	.0744	1540 ± 50
Allyl alcohol	CH_2	72.9	88.1[b]	.0616	1653 ± 50
Ethylene bromohydrin	Br	76.2	87.60[b]	.0605	1655 ± 50
Ethylene chlorohydrin	Cl	72.0	86.26[b]	.0453	1826 ± 50
Ethyl hydracrylate	$C_2H_5O_2C$	62.2	66.2[b]	.0171	2400 ± 50
β-Nitro-ethanol	NO_2	77.5	83.3[b]	(.0403)	1895
		...	...[c]	(.0119)	2600

[a] 0.335 mole of amino-ethanol, 1.242 moles of water and 0.0955 mole of aldehyde showed 21.8% conversion to acetal in a volume of 54.25 cc.

[b] One mole of the alcohol and 0.091 mole of acetaldehyde showed the per cent. conversion indicated, in the volume given in the preceding column. The per cent. conversion given in the table is the average of from four to seven determinations, including in most cases synthetic and hydrolytic experiments. The individual determinations were within 0.5% of the average.

[c] 0.0505 mole of the acetal was isolated from 0.288 mole of nitro-ethanol and 0.273 mole of acetaldehyde.

stants and increasing values for $-RT \ln K$. There have been included in the table for the sake of comparison the redetermined values for butanol, propanol, ethanol and phenylethanol. (The authors are indebted to Mr. A. E. Broderick for the values for butanol and ethanol.) It is believed that the values of $-RT \ln K$ given in the table are accurate to within plus or minus 50 units for all except the first and last alcohols given. Since it was necessary to treat the hydrochloride of β-amino-ethanol with acetaldehyde in a water solution the conditions of this reaction are not directly comparable with the others given in the table. The values given for β-nitro-ethanol are, at best, approximations.

Certain relations become obvious from a consideration of the values given in the table and a comparison of them with previously published values. The order of the halogens, when substituted in the beta position in ethanol, in decreasing affinity for the acetal reaction is the usual one of iodine, bromine and chlorine. However, iodine is more "positive" than is hydrogen in this case for the value of $-RT \ln K$ is 153 units less than for the unsubstituted ethanol. However, ethylene bromohydrin shows a decrease in affinity as compared with ethanol. Hartung showed that the substitution of bromine in acetaldehyde increased affinity for the acetal reaction. The substitution of ethyl, phenyl or methyl groups in the beta position in ethanol increases affinity for acetal formation. The ethoxy group increases affinity by 144 units while the methoxy group has little or no effect.

Hartung showed that the substitution of the methylene group in acetaldehyde (acrolein) decreased the affinity by about 1700 units. In contrast with this is the fact that the substitution of the methylene group in the alcohol (allyl alcohol) has relatively little effect, only lowering affinity by about 100 units.

The carbethoxy group is quite effective in decreasing affinity, the substitution of this group for a beta hydrogen in ethanol lowering affinity by 860 units.

In general it may be said that substitution in the beta position of ethanol has relatively little effect upon affinity for acetal formation. The effect is only a small fraction of what it would be if the substitution were made on the alpha carbon atom and is in the opposite direction in some cases, as, for example, in the case of phenyl and methyl substitution.

It was not possible to obtain any quantitative data upon the relative reactivities of the alcohols studied. In the case of the halohydrins and the ethyl hydracrylate the amount of catalyst present is modified by the small amount of hydrolysis that takes place. The purest samples of the halohydrins obtainable contain, or soon acquire, a concentration of halogen acid which is several times the very small amounts necessary to catalyze the acetal reaction. The methoxy-ethanol and ethylene chlorohydrin showed about 40% reaction of the acetaldehyde in thirty minutes while the *n*-propyl and phenylethyl alcohols showed a little less than 30% in the same interval. The reactions went from 85 to 90% to completion after several hours. Ethoxy-ethanol was a little slower, while allyl alcohol showed less than 20% reaction in the first thirty minutes. This is rather remarkable since the presence of a double bond in the aldehyde greatly increases reactivity. In general it may be said that the compounds whose rates were followed showed no great differences such as one would find in comparing acetaldehyde and benzaldehyde, for example. The greatest difference in reactivity was between the allyl alcohol and the others investigated.

Summary

The equilibrium points in the reaction of β-amino-ethanol, β-phenylethanol, ethylene iodohydrin, β-ethoxy-ethanol, β-methoxy-ethanol, allyl alcohol, ethylene bromohydrin, ethylene chlorohydrin, ethyl hydracrylate and β-nitro-ethanol with acetaldehyde have been determined. Certain relationships have been pointed out as existing between the constitution of an alcohol and the affinity and reactivity that it manifests in acetal formation. Five acetals not hitherto prepared were obtained.

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[Contribution from the Chemical Laboratory of Carthage College]

THE IDENTIFICATION OF ALKYL AND ARYL HALIDES

By E. L. Hill

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A method for the identification of the primary alkyl bromides and iodides[1] was recently described. This method has now been applied

Table I

New Alkyl and Aryl Mercuric Halides

Mercuric bromide	M. p., °C. (corr.)	Formula	Analysis Calcd., %C	Analysis Found, %C
Sec.-Butyl[2]	39	....	...	...
Cyclohexyl[3]	153	....	...	...
Benzyl[4]	119	....	...	...
[a]Phenyl[5]	276	....	...	...
m-Tolyl[6]	184	....	...	...
n-Nonyl	109	$C_9H_{19}HgBr$	26.50	26.31
n-Lauryl	108	$C_{12}H_{25}HgBr$	32.029	31.90
*Iso*propyl	93.5	C_3H_7HgBr	11.18	11.13
β-Phenylethyl	169	$C_6H_5C_2H_4HgBr$	24.90	24.81
o-Tolyl	168	$CH_3C_6H_4HgBr$	22.64	22.59
[b]*p*-Tolyl	231[7]	$CH_3C_6H_4HgBr$	22.64	22.61

[a] This method is applicable to the corresponding iodide, m. p. 266°, first prepared by Dreher and Otto, *Ann.*, **154**, 109 (1870).

[b] The iodide containing this radical melts at 220° (*ibid.*, p. 173).

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[1] Marvel, Gauerke and Hill, This Journal, **47**, 3009 (1925).

[2] Marvel and Calvary, *ibid.*, **45**, 820 (1923).

[3] Grüttner, *Ber.*, **47**, 1651–1656 (1914).

[4] Wolff, *Ber.*, **46**, 66 (1913).

[5] Hilpert and Grüttner, *Ber.*, **46**, 1686 (1913); Dreher and Otto, *Ann.*, **154**, 111 (1870), recorded 291°.

[6] Michaelis, *Ber.*, **28**, 590 (1895).

[7] Pope and Gibson, *J. Chem. Soc.*, **101**, 736 (1912), found 228°.