

anilides from the pyrazolones substituted in the 4 position were stable, thus permitting the preparation of certain β -amino acids. The hydrogenation of α -aminonitriles to substituted 1,2-diamines has not been generally successful due in part to the ease of hydrogenolysis of compounds of this type.

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RECEIVED JUNE 2, 1933
PUBLISHED OCTOBER 6, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BUFFALO]

The Reaction between Aliphatic Orthoformates and Acetone

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Ethyl orthoformate reacts with acetone in absolute ethyl alcohol solution to yield a compound known as a ketone acetal or ketal



a drop or two of concentrated sulfuric acid or equally effective ammonium chloride, hydrochloric acid or pyridine hydrochloride acting as catalyst.¹

It would seem at first glance that Equation 1 is not needed inasmuch as the ketone could be conceived as reacting with the alcohol, splitting off water which then would react with the ortho ester. Moreover, if it is the orthoformate which reacts, why is the alcohol necessary? To answer these questions and if possible to obtain information as to optimum conditions for the reaction, several runs were made using various solvents and catalysts, in most cases ethyl compounds.

The reagents, acetone, alcohol and orthoformate, were mixed in equimolecular amounts and allowed to stand at the temperature of the room (which was quite constant around 25°) for five to seven days. Where sulfuric acid was used as a catalyst the color of the solution darkened and the temperature rose as much as 10° during the first twenty-four hours. The products were isolated according to Claisen's method.¹

Using the following amounts of reagents with various catalysts the following yields of ketals were obtained: 0.143 mole + 1 drop H₂SO₄, 13%; 0.286 mole + 1.3 g. NH₄Cl, 26%; 0.19 mole + 0.75 g. NH₄Cl, 30%; 0.68 mole + 1 drop HCl, 27%. Omission of the solvent or of the orthoformate gave zero yields. Using equimolecular amounts of isoamyl alcohol as a solvent also gave zero yields. Replacement of the ethyl alcohol by ethyl ether using 1 drop of sulfuric acid as catalyst gave an unchanged yield (13%).

A series of runs was then carried out to determine the applicability of this reaction to the preparation of higher homologs of diethyl ketal.

Equimolecular amounts of acetone, the alcohol and the corresponding orthoformate were used. In each case 0.15 g. of ammonium chloride was used as a catalyst for every

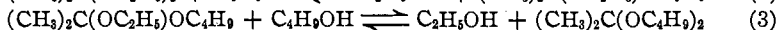
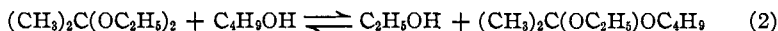
(1) Claisen, *Ber.*, **29**, 1007 (1896); *ibid.*, **47**, 3171 (1914); Arbusow, *ibid.*, **40**, 3303 (1907); Tschischibabin and Jelgasin, *ibid.*, **47**, 48 and 1851 (1914).

hundredth mole of acetone. The amounts of acetone varied between one-tenth of a mole and four-tenths of a mole.

The orthoformates were prepared according to the methods in the literature.²

With propyl alcohol yields of 25–30% of dipropyl ketal were obtained. With butyl, isobutyl, amyl and isoamyl alcohols no ketals were obtained but considerable quantities of orthoformate were recovered (30–50%), the amount varying directly as the molecular weight in a qualitative sense.

Diethyl ketal and butyl alcohol were mixed in molecular proportions of 1:2 and allowed to stand for one week at room temperature and illumination. The products from this reaction were identified as dibutyl ketal and ethylbutyl ketal



No catalyst of any sort was added. Attempts to repeat this reaction with ketal and alcohol involving radicals close to each other in radical weight were unsuccessful because of inability to isolate the pure products. The physical constants of the products were too close together to make identification certain. In this run 10.0 g. of $(\text{CH}_3)_2\text{C}(\text{OC}_2\text{H}_5)_2$ was mixed with 11.2 g. of $\text{C}_4\text{H}_9\text{OH}$. A 16% yield of ethylbutyl ketal resulted, and a 10% yield of dibutyl ketal.

The properties of these ketals are shown in the table. Values for the refractive indices are taken from the literature.³

KETALS

Alkyls	B. p., °C. (mm.)	n_D^{22}	d_4^{22}	Calcd. N, %	Found
Diethyl	112 (736.4)	1.3867	0.820	37.81	37.84
Ethyl, butyl	74–77 (30); 122 (745.9)	1.4049	.867	47.05	45.25
Dipropyl	77 (30); 125 (745.9)	1.4022	.8319	47.05	46.79
Dibutyl	93 (30); 130 (745.9)	1.4084	.824	56.28	56.18

" n " and " d " of diethyl ketal were taken at 21 and 21/4°, respectively.

BUFFALO, NEW YORK

RECEIVED JUNE 2, 1933
PUBLISHED OCTOBER 6, 1933

(2) "Organic Syntheses," **5**, 55 (1925); Sah and Ma, *THIS JOURNAL*, **54**, 2964 (1932).

(3) Landolt and Börnstein, "Physikalisch-chemische Tabellen," Vol. II, 985 (5th ed.).