A CONCISE REVIEW ON SYNTHESIS OF ACETAL AND RECENT ADVANCES

Narayan P. Firke*[1]

[1]*Department of Chemistry, Fergusson College, Autonomous Affiliated to Savitribai Phule Pune University, Pune 411 004, India*

Email address: narayan.firke@fergusson.edu

ABSTRACT

Acetal, a simple, yet an essential functional group recognized in the field of fuel additive, natural oil, flavour and fragrance. The present review sheds some light on the often occurrence and synthesis of acetal and explores acetal as a flavour and fragrance ingredient. This review article includes and emphasizes some of the preparation, industrial, recent green and catalytic methods of synthesis of the generally accepted as safe acetal compounds in concise detail.

Keywords: *Flavours and fragrance, fuel additives, geminal ethers, green chemistry, catalysis, photochemistry.*

1. INTRODUCTION

Acetal[1-3] is formed by the reversible combination of an aldehyde with two molecules of alcohols via the hemiacetal formation process (Figure 1). Acetal is chemically also known as geminal-diether of aldehyde or ketones. Geminal-diether of ketone was once recognized as ketal. however, in modern times merged with the noun acetal. Diol or polyol[4] on reaction with aldehyde or ketone leads to the formation of cyclic acetal through inter-molecular cyclization (Figure 2). The formation of acetal is far standard in carbohydrate and natural products and bears importance in a lot of synthetic as well as biological purposes. Acetal is often used as an excellent protecting group in organic synthesis, wherein the carbonyl group is protected into a non-reactive ether in basic and neutral conditions.[5,6] The use of glycerol acetal and ketal as bio-solvent has been studied along with their volatility and autoxidation stability.[7]

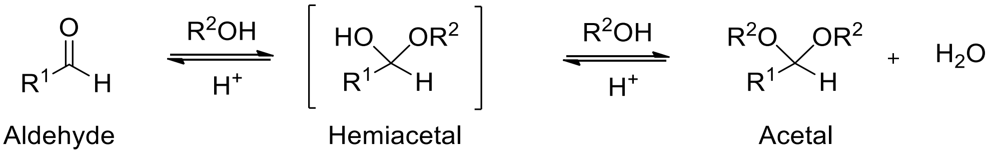

Figure 1: Formation of acetal

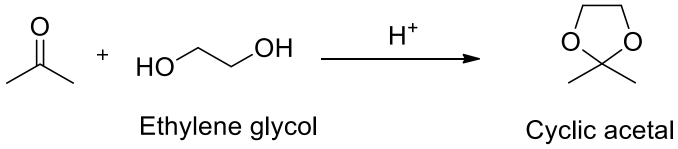

Figure 2: Formation of cyclic acetal

Acetals are the volatile compounds found in vegetal, fermented food, beverages and animal resources essentially contribute to the flavour and fragrance in natural products.[8,9] Acetal compounds have a pronounced effect on our sensory organs and play an important role in defining the quality of flavour[10] and fragrance. Acetal compounds are generally accepted as safe in flavour and fragrance ingredients (Table 1).

Synthesis of Acetal

Acetal, ethoxyethyl ether was prepared with Simmon-Smith reaction[11] Pd/C-catalyzed direct methoxylation of linear benzyl substrate can be converted to acetal in presence of oxygen and *i*-Pr_2Net.[12] Acetaldehyde diisoamyl acetal was obtained as the major side product in ZSM-5/MCM-41 catalysed reaction of vinyl acetate and isoamyl alcohol.[13] Mercuric oxide-iodine reagent on photochemical reaction with 2-(p-iodophenoxy)ethanol reported yielding cyclic acetal mainly ethylene acetal of p-benzoquinone.[14] Novel eleven sulfur containing acetal compounds were synthesis on the basis of observation that meat like flavour expressed by 3-marcapto-butanone.[15]

Table 1: Overview of acetal compounds in flavor and fragrance ingredients

SN	FEMA$ Number	CAS Number	Name of the Compound
1	4273	214220-85-6	(±)-(E)-2-hexen-1-al glyceryl acetal
2	4273	897672-50-3	(±)-(E)-2-hexen-1-al glyceryl acetal
3	4272	94089-21-1	(±)-(E)-2-hexenal propylene glycol acetal
4	4273	897630-96-5	(±)-(Z)-2-hexen-1-al glyceryl acetal[9]
5	4273	897672-51-4	(±)-(Z)-2-hexen-1-al glyceryl acetal
6	4432	25334-93-4	(±)-Acetaldehyde ethyl isopropyl acetal[16,17]
7	4047	67746-30-9	(E)-2-hexenal diethyl acetal[18-20]
8	3426	534-15-6	1,1-dimethoxyethane[20,21]
9	4098	18318-83-7	1,1-dimethoxy-trans-2-hexene
10	4688	105-82-8	1,1-dipropoxyethane[22]
11	4099	3390-12-3	2,4-dimethyl-1,3-dioxolane[23,24]
12	4382	74094-63-6	2,6-dimethyl-5-heptenal propylene glycol acetal
13	3378	67674-36-6	2,6-nonadienal diethyl acetal[25-27]
14	4048	6454-22-4	2-hexyl-4,5-dimethyl-1,3-dioxolane[28]
15	4399	165191-91-3	2-nonanone propylene glycol acetal
16	4595	67634-23-5	2-phenylpropanal propylene glycol acetal
17	2888	90-87-9	2-phenylpropionaldehyde dimethyl acetal[29]
18	3381	5436-21-5	3-oxobutanal dimethyl acetal[30]
19	3349	1192738-48-9	(Z)-4-heptenal diethyl acetal[31]
20	3349	18492-65-4	(E)-4-heptenal diethyl acetal
21	4628	58244-29-4	4-methylbenzaldehyde propylene glycol acetal[32]
22	4400	68258-95-7	6-methyl-5-hepten-2-one propylene glycol acetal
23	2002	105-57-7	Acetal[8,33]
24	4376	202188-43-0	Acetaldehyde 1,3-octanediol acetal[34]
25	3125	64577-91-9	Acetaldehyde butyl phenethyl acetal[34-37]
26	4381	63449-64-9	Acetaldehyde di-cis-3-hexenyl acetal
27	4024	13002-09-0	Acetaldehyde diisoamyl acetal[17]
28	4527	5669-09-0	Acetaldehyde di-isobutyl acetal
29	4528	6986-51-2	Acetaldehyde ethyl isobutyl acetal
30	4365	233665-90-2	Acetaldehyde hexyl isoamyl acetal
31	2004	7493-57-4	Acetaldehyde phenethyl propyl acetal[30,38,39]
32	3775	28069-74-1	Acetaldehyde, ethyl cis-3-hexenyl acetal[40,41]
33	2062	91-87-2	Alpha-amylcinnamaldehyde dimethyl acetal[42]
34	4627	6414-32-0	Anisaldehyde propylene glycol acetal[43]
35	2128	1125-88-8	Benzaldehyde dimethyl acetal[44-47]
36	2129	1319-88-6	Benzaldehyde glyceryl acetal[7,48-58]
37	2129	1708-40-3	[7,48-58]
38	2129	1708-39-0	Benzaldehyde glyceryl acetal[7,48-58]
39	2130	2568-25-4	Benzaldehyde propylene glycol acetal[33]
40	2148	7492-39-9	Benzyl methoxyethyl acetal[30,39]
41	2287	5660-60-6	Cinnamaldehyde ethylene glycol acetal[39,59]
42	4596	4353-01-9	Cinnamaldehyde propylene glycol acetal[17]
43	4286	18433-93-7	Cis- and trans-2-isobutyl-4-methyl-1,3-dioxolane

44	4287	67879-60-1	Cis- and trans-2-isopropyl-4-methyl-1,3-dioxolane
45	2304	7492-66-2	Citral diethyl acetal
46	2305	7549-37-3	Citral dimethyl acetal[60]
47	4486	5694-82-6	Citral glyceryl acetal[17,61]
48	2363	7779-41-1	Decanal dimethyl acetal[39,62]
49	4364	5421-12-5	Decanal propylene glycol acetal
50	4366	14620-52-1	Dodecanal dimethyl acetal
51	3838	68527-76-4	Ethyl vanillin propylene glycol acetal[63,64]
52	4537	4359-54-0	Furfural propylene glycol acetal[17,65]
53	2542	72854-42-3	Heptanal glyceryl acetal (1,2 acetal)[4]
54	2542	1708-35-6	Heptanal glyceryl acetal (1,3 acetal)[4]
55	4368	4351-10-4	Heptanal propylene glycol acetal
56	2541	10032-05-0	Heptanal dimethyl acetal[66]
57	4384	155639-75-1	Hexanal butane-2,3-diol acetal
58	4370	33673-65-3	Hexanal dihexyl acetal[67]
59	4369	896447-13-5	Hexanal hexyl isoamyl acetal
60	4377	202188-46-3	Hexanal octane-1,3-diol acetal
61	2584	7779-94-4	Hydroxycitronellal diethyl acetal[68]
62	2585	141-92-4	Hydroxycitronellal dimethyl acetal[69]
63	4485	93804-64-9	Hydroxycitronellal propylene glycol acetal
64	4371	3842-03-3	Isovaleraldehyde diethyl acetal[70]
65	4380	54355-74-7	Isovaleraldehyde glyceryl acetal
66	4590	16630-61-8	Methional diethyl acetal[17,71]
67	4367	18824-63-0	Nonanal dimethyl acetal
68	4373	68391-39-9	Nonanal propylene glycol acetal
69	2798	10022-28-3	Octanal dimethyl acetal
70	4383	74094-61-4	Octanal propylene glycol acetal
71	4530	121199-28-8	Perillaldehyde propylene glycol acetal[17]
72	2875	5468-06-4	Phenylacetaldehyde 2,3-butylene glycol acetal[36,72]
73	4625	6314-97-2	Phenylacetaldehyde diethyl acetal[73]
74	3384	68345-22-2	Phenylacetaldehyde diisobutyl acetal[36,74]
75	2876	101-48-4	Phenylacetaldehyde dimethyl acetal[75-77]
76	2877	29895-73-6	Phenylacetaldehyde glyceryl acetal[36,78,79]
77	4629	5468-05-3	Phenylacetaldehyde propylene glycol acetal
78	4622	61683-99-6	Piperonal propylene glycol acetal
79	3067	1333-09-1	Tolualdehyde glyceryl acetal (mixed o-, m-, p-)[80,81]
80	4374	74094-62-5	Undecanal propylene glycol acetal
81	4375	13112-65-7	Valeraldehyde dibutyl acetal
82	4372	74094-60-3	Valeraldehyde propylene glycol acetal
83	3904	180964-47-0	Vanillin menthoxypropane-1,2-diol acetal
84	4023	63253-24-7	Vanillin erythro- and threo-butan-2,3-diol acetal
85	3905	68527-74-2	Vanillin propylene glycol acetal[33]

$FEMA: Flavour Extraction Manufacturer Association: *https://www.femaflavor.org/*

Recent Green Synthesis of Acetal

The formation of diethylacetal has been studied in presence of TiO_2 activated under ambient temperature pressure and UV-A atmosphere (Figure 3). The physical form of TiO_2 used in this case was either rutile, anatase or a mixture of both rendering the highest quantum yield of 0.05, the study also found the formation of hydrogen on the surface of TiO_2.[82]

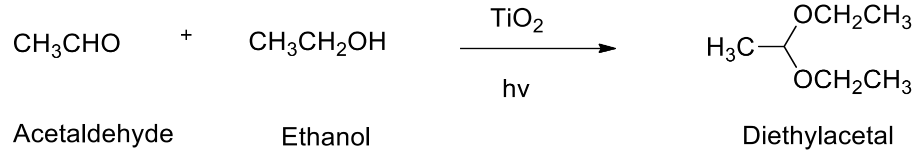

Figure 3: Formation of photocatalytic formation acetal from ethanol

Saha *et al.* reported the chemoselective protection of the aldehyde group in presence of ketone and ester functional group in solvent-free reaction condition (Figure 4). The formation of dioxolane on the catalytic surface of alumina-sulphuric acid.[83] The acid-catalyzed ring opening reaction of methyl 9,10-epoxy stearate, to acetal and ester products, have been studied in solvent-free reaction condition.[84]

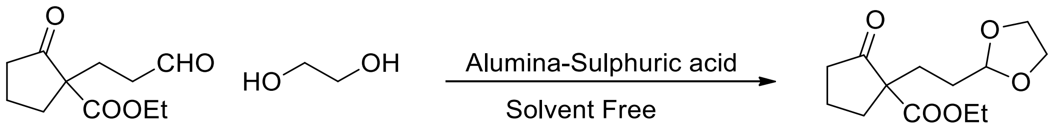

Figure 4: Solvent-free chemo selective protection of aldehyde group

In another green synthesis of acyclic acetal is reported with 75% conversion on the surface of heterogeneous chemoselective Algerian natural kaolin. The kaolin catalyst was well established and characterized by various spectroscopic techniques viz. XRD, FT-IR BET and SEM. This efficient heterogeneous catalyst is used for the first time in organic synthesis and at the same time, it is cost-effective, eco-friendly and can be used for multi-gram scales.[85] A green photochemical protocol was deployed using Eosin Y[86] with green LED, thioxanthenone, [87] Schreiner's thiourea as photocatalyst and household lamps as a light source.[88] A range of aromatic and aliphatic aldehydes was converted into acetals in quantitative high yields (Figure 5).

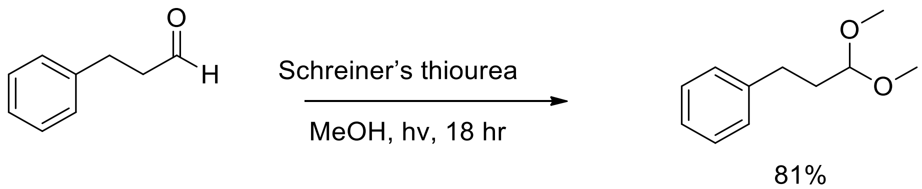

Figure 5: Photochemical synthesis of acetal using Schreiner's thiourea

Catalysts used in the Synthesis of Acetal

Acetals obtained from the glycerol have been the most promising bio-additive fuel,[89] fuel additive.[50] The additives, in this case, are easy to produce at a larger scale. The catalyst p-sulfonic acid calix[4]arene supported by silica ($CX4SO_3HSi(n)$) and can be used in presence of microwave-assisted heating (Figure 6). The reaction was found efficient at the 0.5 mmol of each glycerol and benzaldehyde in presence of a 5% catalyst at 110 degrees Celsius for 20 minutes.[90] The industrial production of acetal from glycerol can be amplified using the flow method.[91] Synthesis of cyclic and linear acetals is achieved by combined utilization of carbon dioxide, hydrogen and biomass-derived diol using Ruthenium catalyst.[92] Styrene was successfully transformed to dimethyl benzaldehyde acetal in presence of $FeSO_4/H_2O_2$ and pyridine-2,6-dicarboxylic acid in 93% conversion yield.[47] Recently, the catalyst Al-SBA-15 has been reported for its excellent catalytic activities in acid-catalyzed glycerol acetalisation including esterification reactions.[55]

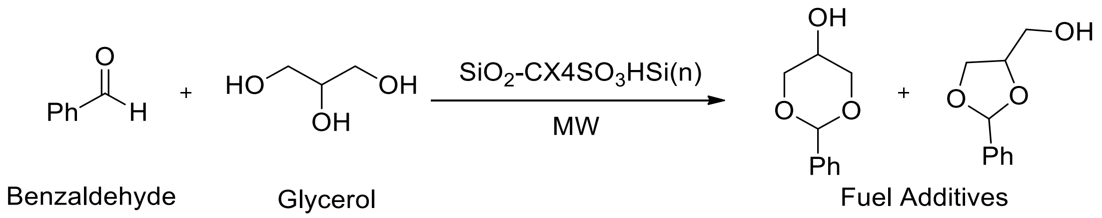

Figure 6: Formation of acetal from glycerol by sol-gel technique

Selectivity in the formation of 1,3-dioxane and 1,3-dioxolane (Figure 7) is one of the important criteria in the usage of acetal as a fuel additive. The highest selectivity in the ratio of 1:99::1,3-dioxane:1,3-dioxolane has been achieved using Fe/Al-SBA-15 with acetone with 51% conversion.[93] Micro mesoporous aluminium silicate nanoparticles were utilized in the synthesis of acetal with propylene glycol.[65]

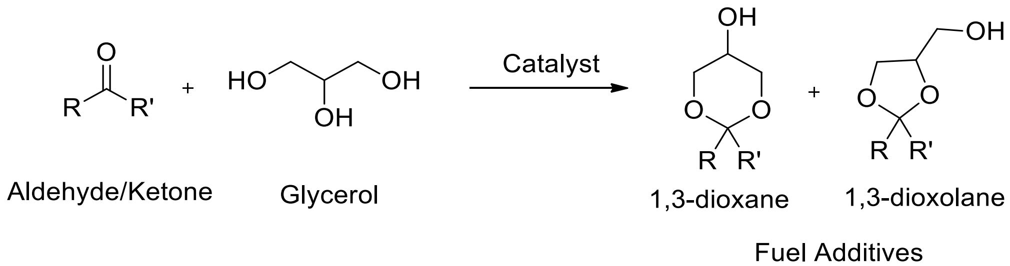

Figure 7: Formation of acetal from glycerol by using different catalysts

Biodiesel is the promising clean fuel of the coming future. Glycerol is the major by-product available from vegetable oil which can be used in the form of acetal as fuel additives.[48] The series of catalyst have been studied chronologically for the conversion of glycerol to fuel additive with different aldehydes and ketones viz. phenylacetaldehyde and zeolite USY-2 (Si/Al = 35),[79] benzaldehyde, formaldehyde and Amberlyst-36,[46] benzaldehyde, p-tert-butyl benzaldehyde, 2-hydroxy,5-nitro benzaldehyde, anisaldehyde, o-chloro benzaldehyde, n-heptaldehyde, n-butyraldehyde, trans-cinnamaldehyde, phenylacetaldehyde, and toluene sulfonic acid, SiO_2, 1% MoO_3/SiO_2, 10% MoO_3/SiO_2, 20% MoO_3/SiO_2,[94] butanaldehyde and Amberlyst-15,[95] formaldehyde and Amberlyst-47,[96] acetaldehyde and Amberlyst-47,[97] benzaldehyde, o-chloro benzaldehyde, p-chloro benzaldehyde, p-anisaldehyde m-nitro benzaldehyde, p-nitro benzaldehdye and $MoO_x/TiO_2–ZrO_2$,[89] paraformaldehyde, acetone, benzaldehyde, furfural and Fe/Al-SBA-15,[93] acetaldehyde, benzaldehyde, acetone and $FeCl_3·6H_2O$,[98] furfural and Montmorillonite-K-10 SC, furfural and Zeolite SBA-15 SC,[99] acetone and VO_xNT, NiVOxNT, CoVOxNT, $PtVO_xNT$,[54] acetaldehyde and SO_4^{2-}/CeO_2 - ZrO_2 catalyst.[58]

Mesoporous Zirconium Oxophospate was efficiently used for the synthesis of cyclic acetal from glycerol and different aldehydes up to 98% practical yields. Using the same catalyst with tetrabutylammonium bromide (TBAB) as co-catalyst various epoxides in combination with carbon dioxide were converted to cyclic acetal.[100] In another study of the green chemistry approach acetylation of aldehyde or ketones was achieved using cyclopentylmethylether in combination with ammonium salts as the solvent/catalyst system. The reactions with this protocol rendered acetals in almost quantitative yield.[101]

Transition elements play an important role in transforming aldehyde or ketone compounds in their respective acetals. Transition element salts or complexes[102] those were used as catalyst for acetalisation are as follows: $Sc(NTf_2)_3$,[103] $TiCl_4$, $Fe(HSO_4)_3$, [Fe(III)]-resin, [Ru], $[Ru_2(CO)_4Cl_2]$, $Cu(BF_4)_2$, $Fe(ClO_4)_3{\bullet}6H_2O$, [Pd], $[(Ph_3PAu)_3O]BF_4$, $Pd(OAc)_2$, $[PdCl_2(MeCN)_2]$, $[AuMe(PPh_3)_3]$, AuCl or $AuCl_3$, [Ru], $[Co_2(CO)_8]$, $[VO(OAc)_2]$, $[Ru(MeCN)_3(triphos)](OTf)_2$, $Cu(OTf)_2$,[104] $[CoH(CO)_4]$, CO, $CoCl_2$, $ZrO(OTf)_2$, $[AuMe(PPh_3)_3]$, $Ph_3AuCl/AgBF_4$, Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl/AgOTf, $PtCl_4$, [In],[105] [Ir], $[Ir(COD)Cl]_2$, MoO_3/SiO_2, Bismuth Triflate,[106] $PdBr_2$,[107] $SnCl_2$¸[108] Sn-®,[109].

Acetals, in general, have been always synthesised in mild acidic conditions, however, Grabowski *et al.* reported an exceptional case wherein the acetal was synthesised in a basic medium (Figure 8) along with sodium alkoxide and corresponding trifluoroacetate ester with quantitative yields.[110]

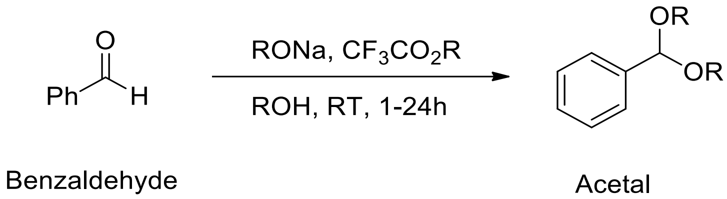

Figure 8: Synthesis of acetal in basic condition

A metal-free catalyst, PTSA, Dowex 50WX8, and Montmorillonite clay, in presence of trichloroacetonitrile for the synthesis of benzylidene acetals were deployed.[111]

CONCLUSION

Synthesis of acetal which is generally accepted as safe in fragrance and flavour can be carried out by a number of catalysts. Researchers have tried transition metals, metal complexes and salts for conversion of aldehyde/ketone compounds to corresponding acetals. The green chemistry approach use of catalysts is clean, efficient, eco-friendly, and cost-effective too.

In acetal synthesis acid heterogeneous and homogeneous catalysts are more commonly used compared to basic medium catalysis, the complementary methods for synthesis of acetal in basic medium with sodium alkoxide and corresponding trifluoroacetate ester with quantitative yields are quite appreciated.

The ratio of 1,3-dioxane and 1,3-dioxolane is an essential criterion in determining the efficacy of fuel additives. Hierarchical micro mesoporous aluminium silicate nanoparticles were used as catalysts in the synthesis of fuel additive acetal.

Rare earth chloride salts are among the good catalyst in the synthesis of acetal. The organic, non-metallic catalyst such as PTSA, Dowex 50WX8, and montmorillonite clay also cannot be ignored for their efficient catalytic activities. Photocatalysis in presence of TiO_2, Schreiner's thiourea, thioxanthenone are ways to get acetal form aldehyde/ketone in almost quantitative yields. The development of heterogeneous catalysts with a higher atom economy would be one of the next challenges in the synthesis of acetal.

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CONFLICT OF INTEREST
The author has no conflict of interest in relation to this work.

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DATA AVAILABILITY STATEMENT
Data sharing is not applicable to this review article as no new data were created or analyzed in this present study.

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