Part II

ORGANIC CHEMISTRY
PHYSICAL PROPERTIES
EVALUATION OF COMPOUNDS AND MATERIALS

Selective Alcoholysis Products of Methyl 9,9-Dimethoxynonanoate

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Various ester-acetal derivatives of azelaaldehydic acid were prepared in good yield by selective alcoholyses of methyl 9,9-dimethoxynonanoate. Transacetalization occurred predominately when alcoholysis was carried out at 75° to 100° for two to four hours in the presence of potassium acid sulfate as catalyst. Transesterification occurred exclusively when alcoholysis was done at about 100° up to 10 hours in the presence of sodium methoxide as catalyst.

METHYL AZELAALDEHYDATE is a versatile chemical intermediate readily available from the ozonization of methyl oleate (*7*, *10*), yet relatively few acetal derivatives have been prepared. Only methyl (*5*), ethyl (*4*) (of the ethyl ester), and pentaerythritol (*11*) acetals have been reported. Pentaerythritol acetals of homologous ω-formylalkanoic acids or their esters—glyoxylic (*1*), malonaldehydic (*1*, *2*), succinaldehydic (*1*), 4,4-dimethyl- and 4,4-diethylglutaraldehydic (*1*) acids—also have been reported. Under certain conditions, the ester group in methyl 9,9-dimethoxynonanoate is stable in the presence of the acidic catalyst used for transacetalization (*12*). The stability of the acetal group is well known under the alkaline conditions used for transesterification. Advantage of these stabilities was taken to prepare a number of different ester-acetal derivatives of azelaaldehydic acid by selective alcoholysis of methyl 9,9-dimethoxynonanoate (I).

TRANSACETALIZATION

Alcoholysis of the acetal group was carried out in the presence of a trace of potassium acid sulfate and an excess of the alcohol (*12*). The mixture was heated at 75° to 100° C. for two to four hours or until methanol, which was removed by distillation, was no longer generated. Crude yields of 80 to 100% were realized, based on gas-liquid chromatographic (GLC) analysis of the crude product before distillation. Hydroxy compounds included *n*-butyl, *n*-hexyl, 2-ethylhexyl, *n*-octadecyl, and allyl alcohols, 2-methoxyethanol, ethylene glycol, pentaerythritol, and glycerol (Table I). Isopropyl alcohol was also used, but it required a heating period of 16 hours at 87° C.

An exception to the selectivity occurred with allyl alcohol. The crude yield of the diallyl acetal was quite low because of two factors: a considerable amount (60%) of

Table I. Ester-Acetal Derivatives of Azelaaldehydic Acid

Compound	Crude Yield, %	Boiling Range, °C./Mm. of Hg	n_D^{30}	d_{20}^{20}	Molar Refractivity		Carbon, %		Hydrogen, %		Sapon. Equiv.	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Methyl 9,9-dimethoxynonanoate (I)	95	86–87/0.13	1.4304	0.9655	62.57	62.12	62.04	61.89	10.41	10.29	232.3	231.0
Methyl 9,9-bis(2-propoxy)nonanoate	71	112–113/0.15	1.4294	0.9263	81.03	80.98	66.70	66.30	11.20	11.07	288.3	289.5
Methyl 9,9-bis(1-butoxy)nonanoate	92	127–129/0.09	1.4344	0.9151	90.26	90.84	68.31	68.20	11.24	11.32	316.5	...
Methyl 9,9-bis(1-hexoxy)nonanoate	95	115–116/0.03	1.4440	0.9046	108.74	108.64	71.25	71.04	11.95	11.79	372.5	369.2
Methyl 8-(1,3-dioxolan-2-yl)octanoate	99	85–85.5/0.05	1.4441	1.0190	60.36	60.51	62.57	62.31	9.63	9.60	230.3	230.8
Methyl 8-(4-hydroxymethyl-1,3-dioxolan-2-yl)octanoate[a]	100	146/0.2	1.4580	1.0741	66.50	66.63	59.97	59.67	9.29	9.33	260.3	260.6
Methyl 9,9-bis(2-ethylhexoxy)nonanoate	89	160/0.05	1.4441	0.8958	127.21	126.17	72.78	72.96	12.18	12.16	428.7	427.7
Methyl 9,9-dioctadecoxynonanoate	80	38.5–39.5[b]	...	...	...	...	78.01	77.77	12.95	12.73	708.5	708.5
Allyl 9,9-dimethoxynonanoate	87	150–153/7.0	1.4399	0.9565	71.33	71.72	65.01	65.33	10.13	10.17	258.7	256.5
2-Ethylhexyl 9,9-bis(1-hexoxy)nonanoate	89	191–192/0.3	1.4526	0.9497	88.86	88.91	69.65	69.28	9.75	9.86	310.4	310.8
2-Ethylhexyl 9,9-bis(2-methoxyethoxy)nonanoate	92.7	...	1.4316	0.9331	76.41	76.78	65.67	65.45	11.02	10.93	274.6	273.6
2-Ethylhexyl 8-(1,3-dioxolan-2-yl)octanoate	88	135–138/0.05	1.4444	0.9816	74.21	73.71	66.13	65.94	10.35	10.46	272.4	272.0
2-Ethylhexyl 9,9-bis(2-ethylhexoxy)nonanoate	81	*ca.* 207/0.06	1.4395	0.9188	94.88	95.70	69.05	68.54	11.59	11.25	330.5	328.4
Ethylene bis(9,9-dimethoxynonanoate)	87	210–213/0.09	1.4474	0.9050	122.59	123.51	72.80	73.13	12.15	11.51	411.0	414.6
Allyl 9,9-diallyloxynonanoate	60	126–128/0.18	1.4483	0.8877	141.06	140.52	74.01	74.10	12.21	11.99	470.7	470.5
Butyl 9,9-dimethoxynonanoate	88	96–97/0.06	1.4439	0.9550	116.64	116.26	66.04	66.08	11.07	10.90	418.2	410.0
Butyl 8-(1,3-dioxolan-2-yl)octanoate	85	115/0.10	1.4488	0.9548	92.68	92.90	69.47	69.73	11.04	11.05	328.5	329.4
2-Ethylhexyl 9,9-dimethoxynonanoate	87	138/0.06	1.4477	0.8975	159.53	158.25	75.25	74.99	12.61	12.55	526.8	525.5
2-Ethylhexyl 9,9-bis(1-butoxy)nonanoate	82	160–161/0.2	1.4477	1.0121	122.91	122.85	62.30	62.45	10.02	10.12	231.3	233.7
Ethylene bis[8-(1,3-dioxolan-2-yl)octanoate]	91	67.5–68.5[b]	...	...	...	...	62.84	63.03	9.21	9.20	229.3	229.8
2,2-Dimethyltrimethylene bis(9,9-dimethoxynonanoate	92.4	...	1.4483	0.9942	136.77	135.80	64.26	64.50	10.38	10.16	252.2	250.5
3,9-Bis[7-carbo(2-methoxyethoxy)heptyl]-2,4,8,10-tetraoxaspiro[5.5]undecane	91	37.5–38.0[b]	...	...	...	...	62.10	61.94	9.37	9.34	280.1	279.5

[a] Probably contains some of the six-membered ring compound, methyl 8-(5-hydroxy-1,3-dioxan-2-yl)octanoate. [b] Melting point (uncorrected).

the diallyl acetal-allyl ester formed and apparent decomposition and rearrangement of the diallyl acetal group occurred (*6, 9*). GLC analysis of the product showed one major peak (the diallyl acetal-allyl ester) and seven minor peaks, which were not identified.

The glycerol acetal was prepared directly from methyl azelaaldehydate (65% yield) as well as from the dimethyl acetal (100% yield). Although optimum conditions were not developed for the direct synthesis, glycerolysis of the dimethyl acetal appears to be much the preferred route. Glycerol acetals have been reported to exist largely in the dioxolane form (*3, 8*).

TRANSESTERIFICATION

Alcoholysis of the ester group was carried out in the presence of sodium methoxide. Heating at 100° C. up to 10 hours was required to obtain yields comparable with those from acetal reactions. For example, compound I (55.3 grams, 0.238 mole), *n*-butyl alcohol (400 ml.), and sodium methoxide (0.12 gram) were heated at 100° in a three-necked, round-bottomed flask fitted with a capillary inlet for nitrogen, a thermometer, and a distillation head. After 10 hours of heating with periodic removal of methanol, the catalyst was neutralized with glacial acetic acid. The product was dissolved in methylene chloride and washed with water until neutral to alkali-acid indicator paper. After drying over anhydrous sodium sulfate, the solvent was stripped off. The yield was 88%, based on GLC analysis. After distillation under reduced pressure, a 75% yield of butyl 9,9-dimethoxynonanoate was obtained; the purity was 99%+ by GLC analysis.

Other hydroxy compounds included 2-ethylhexyl and allyl alcohols, 2-methoxyethanol, ethylene glycol, and neopentyl glycol (Table I).

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Condensation of Cyclohexylacetone with Benzaldehyde, Nitrobenzaldehydes, and Chlorobenzaldehydes

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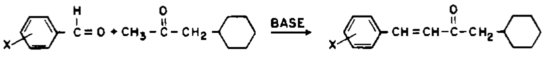
Cyclohexylacetone was condensed with benzaldehyde, *o*-, *m*-, *p*-nitrobenzaldehyde, and *o*-, *m*-, *p*-chlorobenzaldehyde under conditions which favor condensation at the methyl group of cyclohexylacetone. Straight-chain benzylidene ketones were obtained in 63 to 79% yields from all benzaldehydes except from *o*-nitro- and *o*-chlorobenzaldehyde.

AN UNSYMMETRICAL KETONE may undergo condensation at either of the two positions adjacent to the carbonyl group (*3*). To prepare new straight-chain benzylidene ketones from an unsymmetrical ketone, cyclohexylacetone, whose steric hindrance may favor condensation at the methyl group, was condensed with benzaldehyde, nitrobenzaldehydes, and chlorobenzaldehydes.



X = H, *o*-NO_2, *m*-NO_2, *p*-NO_2, *o*-Cl, *m*-Cl, *p*-Cl

The use of a base catalyst and a long reaction time were considered as factors which would favor the formation of straight-chain benzylidene ketone.

In a typical experiment, 14 ml. of cold aqueous sodium hydroxide (10%) was added to a benzaldehyde (0.05 mole) and excess cyclohexylacetone (0.071 mole) in 150 ml. of 95% ethanol. After the mixture stood for several days in the cold (2° C.), crystalline straight-chain benzylidene ketones, I-VI (Table I), precipitated. The attempted condensation of *o*-chlorobenzaldehyde with cyclohexylacetone gave only an oil.

The IR spectra of I-VI show the characteristic carbonyl (1700-1690 cm.$^{-1}$) and olefin (1670-1660 cm.$^{-1}$, 1625 cm.$^{-1}$