# Aldehyde Cotrimers

O. C. DERMER AND ALFRED M. JENKINS

*Received December 12, 1958*

Whereas the trimerization of individual aliphatic aldehydes is a familiar reaction, the formation of mixed trimers has received no systematic study. It has now been found that cotrimerization is a general reaction also, and that the suggestion[1] that aldehyde cotrimers must always contain at least one halogenated aldehyde unit is invalid. Binary mixture of individually polymerizable aldehydes are largely converted by acid catalysts to a mixture of two symmetrically substituted and two unsymmetrically substituted 1,3,5-trioxanes; under favorable circumstances the several trimers can be separated by fractional distillation.

The products obtained are shown in Table I. Since purity and not yield was stressed in fractionation, the yields shown are minimal and of little significance. Attempts to isolate cotrimers of formaldehyde with acetaldehyde and with propionaldehyde failed, but this is attributed to difficulties in separation rather than to failure of the reaction. As might have been expected, acetaldehyde formed no cotrimer with acetone or benzaldehyde.

TABLE I

ALDEHYDE COTRIMERS

| RCHO + R′CHO Used, Moles | Substd. Trioxane Obtained[a] | Yield, G. | B.P., °C./mm. | *d* at *t*, G./Ml. | $n_D$ at *t* | *t*, °C. |
|---|---|---|---|---|---|---|
| 2 MeCHO + 4 EtCHO | 2,4-$Me_2$-6-Et | 60 | 139.5/745 | 0.976 | 1.4098 | 20 |
| | 2,4-$Et_2$-6-Me | 16 | 155.5/745 | 0.961 | 1.4131 | 20 |
| 2.6 MeCHO + | 2,4-$Me_2$-6-Pr | 8 | 96/80 | 0.953 | 1.4141 | 20 |
| 3.0 PrCHO | 2,4-$Pr_2$-6-Me | 42 | 121/69 | 0.932 | 1.4208 | 20 |
| 3.3 MeCHO + | 2,4-$Me_2$-6-*iso*-Pr | 46 | 97/140 | 0.939 | 1.4060 | 31 |
| 1.4 *iso*-PrCHO | 2,4-(*iso*-Pr)$_2$-6-Me | 14 | 113/131 | 0.923 | 1.4150 | 29 |
| 1.8 MeCHO + | 2,4-$Me_2$-6-*n*-$C_6H_{13}$ | 21 | 102–103/11 | 0.917 | 1.4214 | 30 |
| 1.3 *n*-$C_6H_{13}$CHO | 2,4-(*n*-$C_6H_{13}$)$_2$-6-Me[b] | 12 | 164/11 | 0.895 | 1.4337 | 27 |
| 1.7 EtCHO + | 2,4-$Et_2$-6-Pr | 14 | 138–139/165 | 0.917 | 1.4156 | 26.5 |
| 2.5 PrCHO | 2,4-$Pr_2$-6-Et | 19 | 128/55 | 0.918 | 1.4192 | 28 |
| 2.7 MeCHO + | 2,4-$Me_2$-6-$EtOC_2H_4$[b] | 13 | 96/17 | 0.996 | 1.4202 | 25.5 |
| 0.8 $EtOCH_2CH_2CHO$ | 2,4-($EtOC_2H_4$)$_2$-6-Me[b] | 11 | 141–142/14 | 1.000 | 1.4294 | 24 |
| 1 MeCHO + 1 PrCHO + 1 *n*-$C_6H_{13}$CHO | 2-*n*-$C_6H_{13}$-4-Me-6-Pr[c] | 8 | 122/10 | 0.913 | 1.4289 | 22 |
| 3.6 MeCHO + 1.2 $CH_2$:CHCHO | 2,4-$Me_2$-6-vinyl[d] | 5 | 138–140/745 | 1.000 | 1.4199 | 26.5 |
| 1.8 MeCHO + 1.1 MeCH:CHCHO | 2,4-$Me_2$-6-(1-propenyl)[e] | 9 | 94/40 | 0.983 | 1.4301 | 29 |

[a] Purity was established for each by showing agreement of calculated and observed values for carbon and hydrogen content (except as noted), molecular refraction, and molecular weight. [b] No carbon-hydrogen analysis. [c] Other products were not sought. [d] Bromine number according to J. B. Bradstreet and R. B. Lewis, *Ind. Eng. Chem., Anal. Ed.*, **12**, 387 (1940): Calcd., 111; Found, 73. This and the results of analysis for hydrogen (Calcd., 8.39%; Found, 8.98%) suggest that the compound was very pure. [e] Bromine number: Calcd., 101; Found, 99.

The formation of the cotrimer containing three different aldehyde units is of particular interest since Hibbert, Gillespie, and Montonna[2] were unable to obtain such compounds from halogenated aldehydes.

A few trials of 2,4-dimethyl-6-ethyltrioxane as a hypnotic by hypodermic injection in rats showed it to be quite toxic, lacking the safety margin of paraldehyde. This extends the observation of Knoefel[3] that other symmetrical trialkyltrioxanes are inferior to paraldehyde. We are indebted to Dr. A. A. Hellbaum and Mr. Dwight L. Smith of the University of Oklahoma School of Medicine for the pharmacological tests.

## EXPERIMENTAL

Reagent grade or redistilled technical grade aldehydes were mixed, chilled in an ice bath, and treated with a small stream of hydrogen chloride for several seconds. The solution was stirred briefly, kept in a closed container in the ice bath for several hours, and then poured into aqueous potassium carbonate. The nonaqueous layer was dried over potassium carbonate and fractionally distilled, usually in either an Oldershaw or a Todd column. It consisted almost entirely of monomers and trimers; very little viscous or solid product was obtained.

DEPARTMENT OF CHEMISTRY
OKLAHOMA STATE UNIVERSITY
STILLWATER, OKLA.

---

[1] J. C. Bevington, *Quart. Rev.*, **6**, 141 (1952).

[2] H. Hibbert, W. F. Gillespie, and R. E. Montonna, *J. Am. Chem. Soc.*, **50**, 1950 (1928).

[3] P. K. Knoefel, *J. Pharmacol.*, **48**, 488 (1933).