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FREE RADICAL ADDITION OF 1,3,5-TRIOXAN TO OLEFINS

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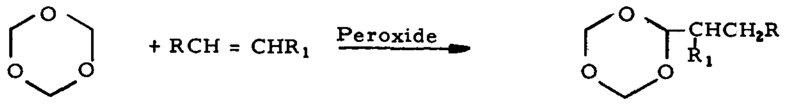
In a recent publication (1) we have reported the light-induced addition of acetals to olefins which led to the corresponding monoalkyl acetal derivatives. We report now the peroxide-induced addition of 1,3,5-trioxan to olefins at elevated temperatures.



($R=C_3H_7$, $R_1=H$; $R=C_6H_{13}$, $R_1=H$; $R=C_8H_{17}$, $R_1=H$; $R=C_{10}H_{21}$, $R_1=H$; $R=R_1=COOC_2H_5$)

This addition reaction was induced with di-t-butyl-peroxide at 115° (48 hr) with a 1,3,5-trioxan:olefin:peroxide ratio of 10:1:1, respectively. The experimental results and major products obtained are summarized in the Table.

TABLE

Addition Products of 1,3,5-Trioxan and Olefins

Olefin	Product[a]	Yield[b] %
Pent-1-ene	Pentyl-1,3,5-trioxan[2]	10
Oct-1-ene	Octyl-1,3,5-trioxan	20
Dec-1-ene	Decyl-1,3,5-trioxan	20
Dodec-1-ene	Dodecyl-1,3,5-trioxan	25
Diethyl Maleate	Diethyl (1,3,5-trioxanyl)-succinate	51

[a] All compounds gave satisfactory analytical results.

[b] Yields are based on the olefins employed.

The products were isolated by chromatography on alumina and characterized by elemental analyses, infrared and n.m.r. spectra. Hydrolysis of the adducts with dilute mineral acids gave formaldehyde and the corresponding higher aldehydes which were characterized through their 2,4-dinitrophenylhydrazones.

It is noteworthy that cyclic acetal free radicals, which usually tend to decyclize at elevated temperatures (3), were in the present case scavenged by olefins before undergoing decyclization, to give 1:1 adducts. The present reaction thus provides a method for the synthesis of monoalkyl-1,3,5-trioxans, until recently unknown (1).

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References

(1) I. Rosenthal and D. Elad, *J.Org.Chem.*, *33*, 805 (1968).

(2) Pentyl-1,3,5-trioxan, m.p. 11-13° (*n*-pentane). N.m.r. ($CDCl_3$, TMS internal): a multiplet centered at τ 4.85 (5H, $-O\underline{CH_2}O\underline{CH}O\underline{CH_2}-$), a broad signal at τ 8.7 [8H, $-(\underline{CH_2})_4-CH_3$] and a triplet at τ 9.1 (3H, $-\underline{CH_3}$). The physical and spectroscopic data of other compounds have been described elsewhere (1).

(3) L.P. Kuhn and C. Wellman, *J.Org.Chem.*, *22*, 774 (1957); E.S. Huyser, *ibid*, *25*, 1820 (1960); C.L. Aldrige, J.B. Zachry, and E.A. Hunter, *ibid*, *27*, 47 (1962); E.S. Huyser and Z. Gracia, *ibid*, *27*, 2716 (1962); E.S. Huyser, R.M. Kellog and D.T. Wang, *ibid*, *30*, 4377 (1965); E.S. Huyser and D.T. Wang, *ibid*, *29*, 2720 (1964).