

The Formation of 3-Methyloctan-4-one and Polyketones by the Oxo Reaction of Butadiene

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It has previously been established that nonan-5-one, together with *n*- and isovaleraldehyde, is formed by the oxo reaction of butadiene catalysed by dicobalt octacarbonyl,^{1,2)} but neither branched-chain C₉-ketone nor polyketones.

We have found that 3-methyloctan-4-one (I) and polyketones (C₄H₉... (CC₄H₈)_n... C₄H₉) (II)



are also formed by the oxo reaction of butadiene.

The reaction of butadiene (8.1 g) with synthesis gas (H₂/CO=1.3: initial pressure, 230 kg/cm² at room temp.) was carried out at 165±5°C for 2 hr in a stainless-steel autoclave (100 ml) using cyclohexane (30 ml) as the solvent and dicobalt octacarbonyl (0.68 g) as the catalyst.

The gas chromatogram of the reaction products showed the presence of Compound I (0.77 g), which had a retention time near to that of nonan-5-one, and several compounds of a longer retention time in addition to the previously-known products (*n*-C₅-aldehyde: 1.34, iso-C₅-aldehyde: 0.75, *n*-C₅-alcohol: 0.33, iso-C₅-alcohol: 0.15, nonan-5-one: 1.48 g). A white, waxy material, II (4.6 g), was separated from the reaction products by the addition of aqueous methyl alcohol after the decobaltation.

The IR spectrum of I showed the existence of a carbonyl group (1715 cm⁻¹). The NMR spectrum, measured in CDCl₃, with tetramethylsilane used as the internal standard, showed bands at 9.1 (multiplet, -C-CH₃, 6H), 8.9 (doublet, -C-CH₃,



3H), 8.6 (multiplet, -C-CH₂-C-, 6H) and 7.6 τ (multiplet, C-CH-C-, 3H). Found: mol wt 142



(by mass spectrum). Calcd for C₉H₁₈O: mol wt 142. It was concluded from these results that I was 3-methyloctan-4-one.

The IR spectrum of II was essentially identical with that of I in the NaCl region. The NMR spectrum of II showed bands at 9.1 (broad, -C-CH₃,

22% H), 8.5 (broad, -C-CH-C-, 43% H) and 7.9 τ (broad, -C-CH-C-, 35% H). Found: C, 72.60:



H, 10.90%: mean mol wt 1180 (V.P.O. in benzene). Calcd for (C₆H₁₁O)_n: C, 72.8; H, 10.6%. The IR and NMR spectra showed no peaks characteristic of C=C, ester, aldehyde, or carboxylic acid. It was concluded from these results that II was mainly a mixture of polyketones, C₄H₉... (CC₄H₈)_n... C₄H₉,



in which carbonyls were not always inserted regularly.

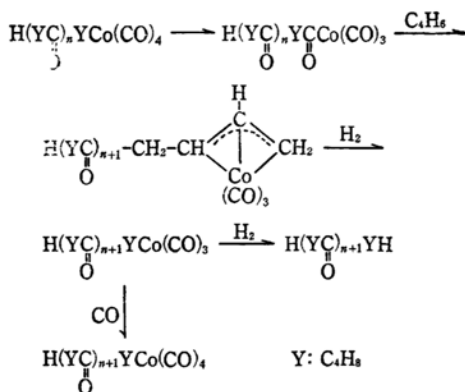
The yield of polyketones increased with the amount of charged butadiene under the same reaction conditions (Table 1).

TABLE 1. THE YIELD OF PRODUCTS (g)*1

Charged butadiene	5.4	8.1	10.8	13.5	16.2
C ₅ -aldehyde (<i>n</i> +iso)	1.81	2.09	2.40	1.94	0.41
Nonan-5-one	1.07	1.48	2.15	2.43	0.68
3-Methyloctan-4-one	0.40	0.77	1.16	1.50	0.24
Polyketones	0.4	4.6	7.3	9.5	14.5

*1 The reaction conditions were similar to that described in the example.

The reaction scheme of the formation of polyketones may be represented as follows:



Detailed studies are now in progress.

1) H. Adkins and J. L. R. Williams, *J. Org. Chem.*, **17**, 980, (1952).

2) J. A. Bertrand, C. L. Aldridge, S. Husebye and H. B. Jonassen, *ibid.*, **29**, 790 (1964).