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Dimerisation and Oligomerisation by Dehydrogenation as a General Synthetic Principle (1a) Part II

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Summary

Capto-dative substituents determine the ease of selective hydrogen abstraction but steric factors and the nature of the dehydrogenating agent influence the relative "radical scale". This study underlines the preparative value of dehydrodimerisations. This method allows in addition the preparation of oligomers and polymers. A continuation of this work will be published in the near future. – – –

The dehydrodimerisations generally succeed best in neat phase. The reaction temperatures with di-tert-butyl peroxide (DTBP) as oxidant is above 140°C using for example 1 mole of oxidant for 20 moles of substrate in a sealed tube or in an autoclave.

Table 1 shows the oxidative dimerisation of esters, amides and analogous compounds with DTBP. The oxidative dimerisation of disubstituted methanes is shown in Table 2.

TABLES 1 TO 2

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TABLE 1

Oxidative dimerisation of esters, amides and analogous compounds with DTBP

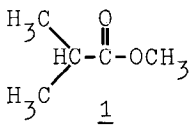
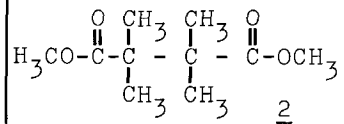
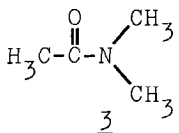
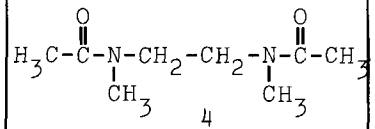
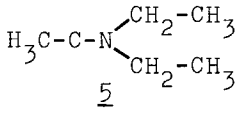
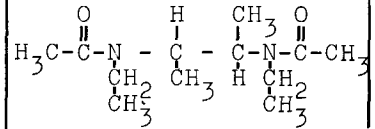
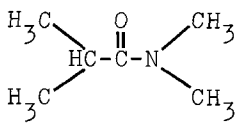
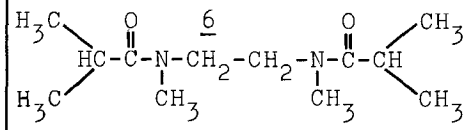
MONOMER	DIMER	YIELD[a]	OTHER METHODS		OTHER DIMER SYNTHESES	
			Yield		Ref.	Selected Refs.
 1	 2	76	2	Fenton's reagent	1	3
 3	 4	100	85	DTBP	4	5
 5		75[b] (62)				
 7	 8	75 (62)				

TABLE 1 (continued)

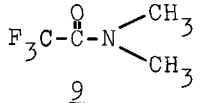
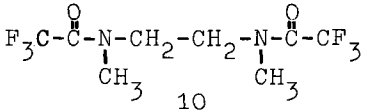
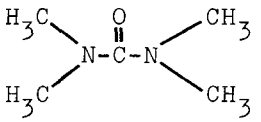
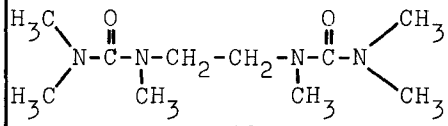
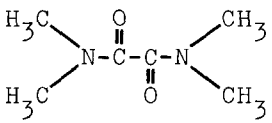
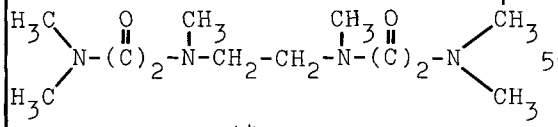
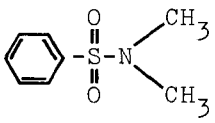
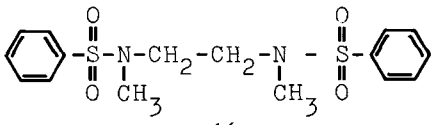
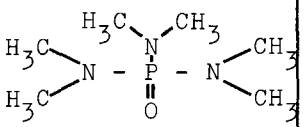
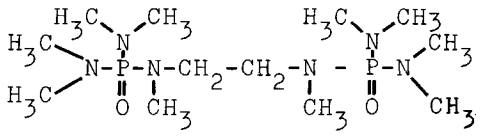
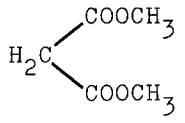
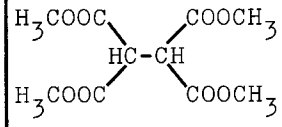
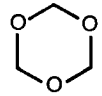
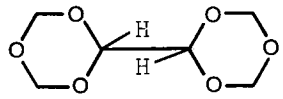
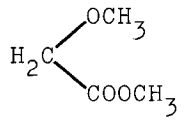
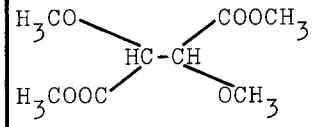
 9	 10	100 (62)		
 11	 12	92		7
 13	 14	56		
 15	 16	78		8
 17	 18	86		9

TABLE 2

Oxidative dimerisation of disubstituted methanes with DTBP

MONOMER	DIMER	YIELD[a)]	OTHER METHODS		OTHER DIMER SYNTHESES	
			Yield		Ref.	Selected Refs.
 19 (=6 in Part I)	 20	59			10	11
 21	 22			ketone, irrad.	12	
 23 (= 4 in Part I)	 24 (= 5 in Part I)	91				13

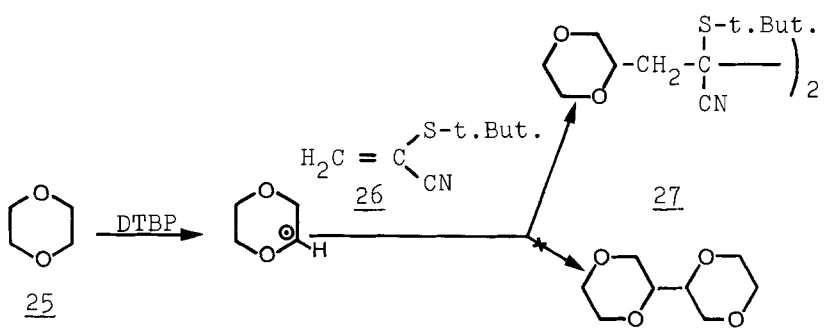
The dimerisation and oligomerisation of dioxane 25 with different oxidants have been examined (see Table 3) as well as the influence of the molar ratio of substrate to oxidant (see Table 4) and the variations of the temperature (see Table 5).

TABLES 3 TO 5

Dehydrodimerisation of isopropyl derivatives (Table 6) such as cumene (15) lead to thermally unstable tetraalkylethane derivatives. These are therefore useful compounds, for example as radical initiators and flame retardants. In particular, imide dimers are as efficient as dicumyl.

TABLE 6

In conclusion, it appears that the age-old oxidative coupling can be seen in a new light as a valuable and promising method of laboratory and industrial C - C bond formation. Use of this principle combined with radicophilic olefins 26 even lead to the "C4 bridged dehydrodimers" such as 27, whereas simple dehydrodimerisation is completely suppressed. (14,16)



Transition metal oxides and peroxides have also been used. Since stoichiometric quantities of oxidants are needed, catalytic systems which use the oxygen of the air with catalysts such as salcomine or molybdates are particularly attractive (see the following table).

TABLE 3

Dehydrodimerisation of dioxane with various oxidants[a)]

Oxidant	Yield[b)] %
HgO	26
Pb O_2	55
Pb O	12
Salcomine/O_2 complex	52
Ammonium molybdate	20
Ni-peroxide	44
DTBP	77
Air	-

a) 1 mole oxidant to 10 moles dioxan 25, 150°C, 5 h., in fluid bed in presence of air (20 l/hour), taking air alone, no dimerisation occurs.
b) Relative to applied oxidant.

TABLE 4

Influence of the dioxane/DTBP ratio on the oligomer distribution at 160°C

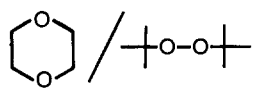
Molar ratio 25 	Distribution of oligomers di- tri- tetra- oligomers				Yield %
20 : 1	95	5			80
20 : 5	50	40	10		85
20 : 10		40	35	5	96

TABLE 5

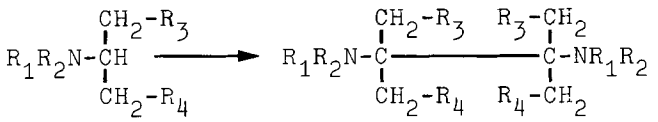
Influence of the temperature on the dimerisation of dioxane[a)]

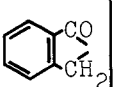
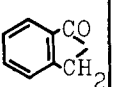
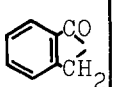
	Di-	Tri-	Tetra-	Oligomers	Yield
160°C	95	5	-	-	80
180°C	90	5	5	-	85
190°C	90	5	5	2	90
200°C	80	10	5	5	95

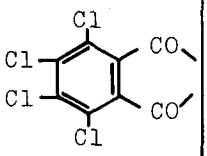
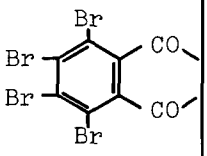
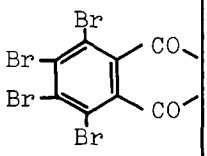
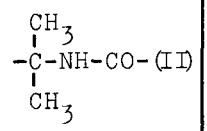
a) Molar ratio of dioxane/t.-But. peroxide = 20 : 1

TABLE 6

Dimerisation of N-tertiary alkyl compounds



No.	R_1R_2	R_3	R_4	Decomposition temperature (°C)	Mol. weight[a]	Yield[b] (%)
28		H	H	approx. 150	280 (295)	82
29		CH_3	H	approx. 140	308 (320)	80
30		H	H	approx. 150	284 (265)	72
31		CH_3	H	approx. 140	280 (296)	65
32		CH_3	OH	approx. 190	312 (325)	52
33		H	H	> 200	348 (340)	74
34		CH_3	OH	> 250	380 (396)	56
35		CH_3	H	approx. 190	376 (384)	78
36		H	H	> 200	344 (355)	82
37		CH_3	H	approx. 200	372 (390)	85

No.	R_1R_2	R_3	R_4	Decomposition temperature (°C)	Mol. weight[a]	Yield[b] (%)
38		H	H	> 250	625 (680)	64
39		H	H	approx. 230	1008 (-)	79
40		CH_3	H	approx. 200	1036 (-)	62
41		H	H	> 250	286 (280)	55
42	NH_2-CO-(II)	H	H	> 220	202 (215)	48

a) In parentheses: Mol. weights determined by cryoscopy in dioxane or dimethylformamide.

b) % = percentage by weight

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