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

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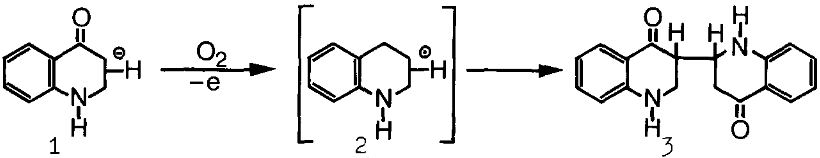
Dedicated to Professor Dr. Matthias Seefelder on the occasion of his 60th birthday

Summary

Donor or acceptor groups and particularly 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 industrial synthesis of indigo by dehydrodimerisation of oxindol is a classical example of radical coupling(10) as a reaction type on which this publication focusses:



1 Anion

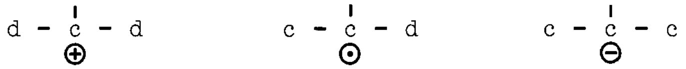
Indoxyl

2 Radical

3 Leuco-indigo

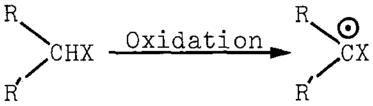
0170-0839/80/0002/0363/$02.00

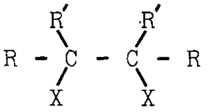
Dehydrodimerisation now appears to us in a new light as a general synthetic method of dimerisation in view of the concept of capto-dative radical stabilization.(2) Because of their electronic situation between cations (stabilized by donors) and anions (stabilized by acceptors), radicals enjoy a particular stabilization by geminal substitution with both a donor (d) and an acceptor (c) group.



The oxidation of cd-methylene compounds such as oxindol led us to a more general comparison with other substitution types.

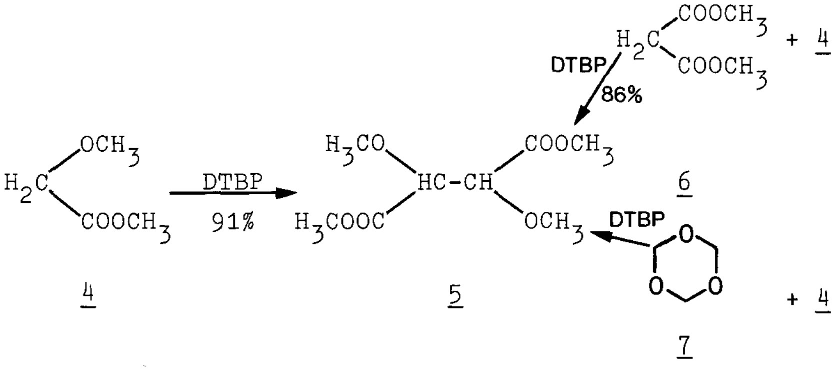
By the pioneering work particularly of Kharash(3) and of (3,38) Schwetlick (4), it is well known that oxidative dimerisation via radicals can be applied to different classes of compounds such as electron rich ethers or amines and electron poor ketones, esters or nitriles (5).





X = OR, NR_2, COR, CN, etc.

Even paraffins (4,6) can be applied to this reaction but donor or acceptor substituents permit a selective oxidative radical dimerisation in the α-position. It appears now that capto-dative substitution on a methyllene group renders this site still more pro-radical than the substitution by two donor or two acceptor substituents, for example:



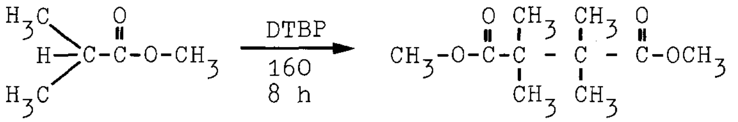
4

5

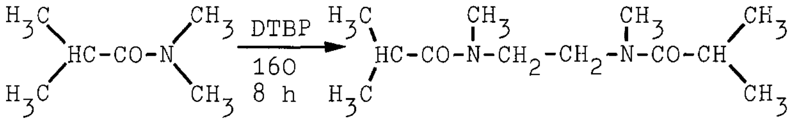
6

7

While a radical scale appears to emerge from competition experiments (7,8), the synthetic potential of dehydrodimerisation appears to be not yet fully recognised, for example in textbooks. This reaction type represents, however, one of the easiest and neatest ways of C-C bond formation, in which high selectivity can be achieved. Thus, whereas the ester 8 dimerises in a position to the carbonyl group, the amide 10 does it rather in a position to the nitrogen, although in 8 the radical is formed on tertiary and in 10 on the primary carbon.



8 9 (76%)



10 11 (75%)

A quantitative study is necessary in order to establish whether these couplings reflect the relative thermodynamic stability of the intermediate radicals. Certainly polar and steric factors of both the oxidising agent and its partner are involved in the kinetics of the oxidative dimerisation. While these contributions still remain to be evaluated the now reported high yields show that the already classical method of dehydrodimerisation merits new attention.

The dehydrodimerisations generally succeed best in neat phase. The reaction temperatures with di-tert-butyl peroxide (8) (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.

TABLES 1 TO 2

TABLE 1

Oxidative dimerisation with DTBP in α-position to donor groups

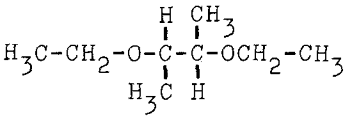
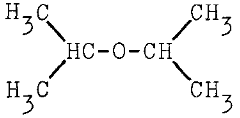
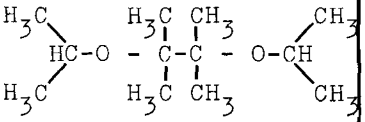
			OTHER DEHYDRODIMERISATIONS		OTHER SYNTHESES OF THE DIMERS	
MONOMER	DIMER	YIELD[a)]	Yield	Method	Ref.	Selected Refs.
CH_3-OCH_3	$H_3C-O-CH_2-CH_2-OCH_3$	64		UV-photolysis (Hg sensitive)	9	11
12	13			pyrolysis	10	
$H_3C-CH_2-O-CH_2-CH_3$	 $H_3C-CH_2-O-\overset{H}{\underset{H_3C}{C}}-\overset{CH_3}{\underset{H}{C}}-OCH_2-CH_3$	58[b)]	46	DTBP	4	
				γ-radiolysis	12	
				1,4-bis (diazomethylbenzene)		
14	15			UV photolysis	14	17
				CH_3COCl photolysis	15	
				Et 3-Me-3-phenyl glycidate, photolysis	16	
		73		$HgCl_2$, photolysis	13	
16	17					

TABLE 1 (continued)

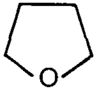
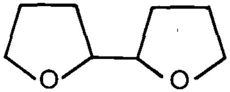
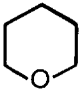
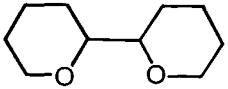
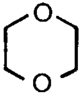
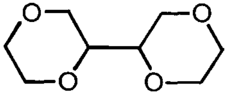
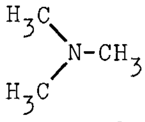
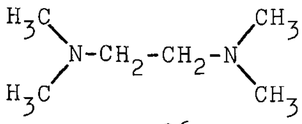
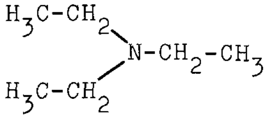
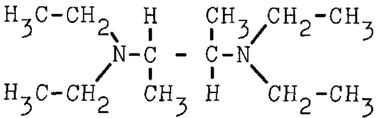
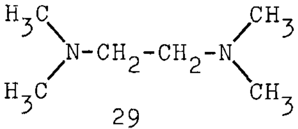
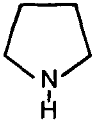
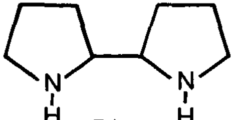
 18	 19	$79^{b)}$		acetone, MEK photolysis 1,4-bis (diazo-methylbenzene), UV photolysis $HgCl_2$, photolysis 1-Ethoxy-7-norbornyl bromide, Mg	18 19 14 13 20	21
 20	 21	$80^{b)}$		$HgCl_2$, photolysis	13	22
 22	 23	$77^{b)}$	12	UV-photolysis photolysis UV or γ-rad. perester, UV acetone, photolysis $HgCl_2$ H_2O, 2-(morpholino-methyl) phenol, photolysis	23 24,25 26 27,28 18 13 29	
$H_3C-O-CH_2-CH_2-O-CH_3$ 24	Mixture of dimers$^{c)}$	100	3			

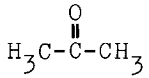
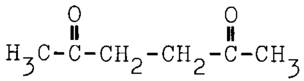
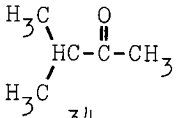
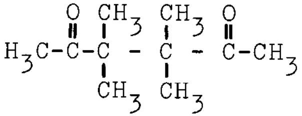
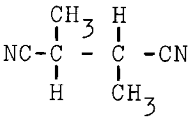
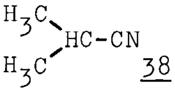
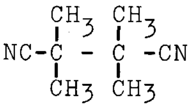
TABLE 1 (continued)

 25	 26	60	60	DTBP γ-radiolysis	4 30	31,32,33
 27	 28	$69^{b)}$	25 10	DTBP UV-photolysis γ-radiolysis photolysis	4 34 35 36	
 29	Mixture of dimers$^{d)}$	13				
 30	 31	$73^{b)}$				

a) Relative to DTBP
b) Mixture of meso- and DL isomers
c) All possible isomers are present

TABLE 2

Oxidative dimerisation with DTBP in α-position to acceptor groups

MONOMER	DIMER	YIELD[a)]	OTHER DEHYDRODIMERISATIONS Yield	OTHER DEHYDRODIMERISATIONS Method	OTHER SYNTHESES OF THE DIMERS Ref.	OTHER SYNTHESES OF THE DIMERS Selected Refs
 $H_3C-\overset{\overset{O}{\|}}{C}-CH_3$ 32	 $H_3C-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$ 33		30	DTBP CuCl$_2$DMF Mn(OAc)$_3$ Fenton's reagent Pyrolysis, photolysis, UV and X rays	4 37 38 39	40
 34	 $H_3C-\overset{\overset{O}{\|}}{C}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\overset{O}{\|}}{C}-CH_3$ 35	79		diacetyl peroxide 5-methyl-1-phenyl 1,2,3-triazole-4-carbonyl peroxide	41 42	44
H_3C-CH_2-CN 36	 $NC-\underset{H}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{H}{C}}-CN$ 37	70[b)]	23	Ni-peroxide CuCl$_2$, DMF DTBP	43 37 4	45
 38	 $NC-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CN$ 39	84			46 47	48

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