Tetrahedron Letters,Vol.24,No.4,pp 385-388,1983 0040-4039/83/040385-04$03.00/0
Printed in Great Britain

REGIO AND STEREO SELECTIVE SYNTHESIS OF DISUBSTITUTED CYCLOOCTADIENES.

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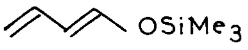
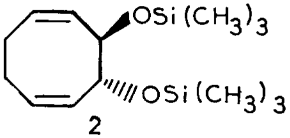
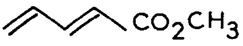
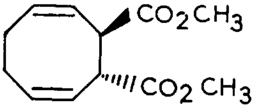
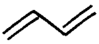
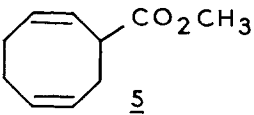
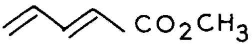
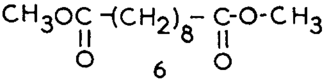
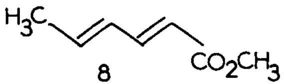
Summary : Functionnalized dienes can be dimerized in the presence of Ni(o) catalyst in order to afford regio and stereo selectively 1,2-trans disubstituted 3,7-cyclooctadienes derivatives.

The formation of medium size ring (8 to 11 membered) is known to be difficult even under Ziegler high dilution conditions (1). Among these, cyclooctane derivatives are of particular interest (2) and it has been known since the pioneering work of Wilke that such products can be obtained by cyclooligomerisation of butadiene on Ni(o) catalysts. However such cyclodimerisation has been studied mainly in the case of alkyl substituted dienes. Furthermore to render this process unequivocal it is necessary to carefully control the reaction conditions and particularly the nature and amount of added ligands (3).

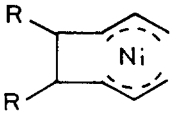
We have recently developped the concept of internal ligand (4) in which a polar substituent of functionnalized dienes can interact with the metal used as catalyst and thus act as a ligand. Such a concept has been used in order to control the selective cyclodimerisation of substituted butadienes. Our results are reported below (fig.I) and show that the dimerisation of such butadiene units can be efficiently controled by the choice of appropriate substituents in such a way that exclusive formation of regioselectively and stereoselectively substituted cyclooctadienes is observed. Easily obtainable dienes such as 1-trimethylsiloxy 1,3 butadiene 1 (5), methyl-2,4 pentadienoate 3 (6) and acetoxy-1,3 butadiene 7 (7) have been used as starting material. The cyclization was carried out with Ni(o) obtained either by reduction of Ni(acac)$_2$ by Et$_2$AlOEt in presence of PPh$_3$ as ligand or with preformed Ni(COD)$_2$ without added ligands. Similar results were obtained with these two catalytic systems. The reactions were performed under Argon with benzene as solvent. When the reaction was successful exclusive formation of trans disubstituted, 1,5-cyclooctadiene was observed. Structure of these compounds was determined by spectroscopic methods and chemical degradation (8,9).

FIGURE I

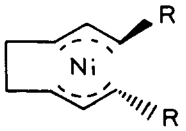
Entry	Compound	Catalyst	Product	Reaction time	Yield
1	 1	Ni(0)	 2	18 d	90 %
2	 3	Ni (0)	 4	24 h	70 %
3	3 + 	Ni (0)	 5	72 h	33 %
4		1) $Pd(OAc)_2$ 2) H_2 Pd/C	 $CH_3OC(=O)-(CH_2)_8-C(=O)-OCH_3$ 6	18 h	77 %
5	 7	Ni (0)	unchanged		
6	 8	Ni (0)	unchanged		

There is a marked influence of electron withdrawing groups on the reaction kinetic such as an ester compared with an electrondonating group. With an acetate as substituent (see entry 5) the reaction is unsuccessful probably because of an oxidation of nickel zero into $Ni(OAc)_2$ similar to the one reported by Yamamoto (12). Obviously the dimerisation is also sensitive to steric hindrance (entry 6). Monosubstituted cyclooctadienes can be obtained by cross coupling between butadiene and functionnalized dienes (3) (see entry 3) but the yield is low as they are formed along with the Diels Alder adduct between the diene ester and butadiene ; the latter being in theses conditions, the dienophile (14).

The question was raised to know whether the cyclization occured via an intermediate such as 9 or 10.



9



10

In order to test these hypothesis we submitted the ester 3 to a palladium catalyst where π allyl complexes similar to the ones formed with nickel are likely to be involved (15). After hydrogenation we obtained exclusively the linear diester 6 which shows that an intermediate such as 10 is probably involved. Accordingly reductive coupling of the two butadiene units occurs on the non substituted carbon of the diene units, a situation similar to the one reported by Vollhardt on substituted acetylenes (16). During the formation of the second carbon-carbon bond, the two terminal substituents must be trans in order to minimize the steric interactions in the transition state (17). This factor nicely explains the high stereoselectivty which is observed.

We are presently investigating the synthetic potential of this reaction as well as its mechanistic implications.

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8 - 2 ^{1}H NMR (60 MHz, CDCl$_3$) : 0.19 (s, 9H) ; 2.30 (m, 2H) ; 4.60 (m, 1H) ; 5.56 (m, 2H) IR (neat) : 1687, 1060, 840 cm^{-1} ^{13}C NMR:131.9 (d) ; 127.4 (d) ; 74.4 (d) ; 27.4 (t) ; 0.0 (q).

4 ^{1}H NMR (60 MHz, CDCl$_3$) : 1.70-2.56 (m, 2H) ; 3.42 (s, 3H) ; 3.93 (s, 1H) 5.30 (m, 2H) IR (neat) : 3025, 1735, 1655 cm^{-1} ^{13}C NMR:173.4 (s) ; 129.7 (d) ; 126.1 (d) ; 52.1 (q) ; 46.9 (d) ; 27.8 (t).

6 ^{1}H NMR (60 MHz, CCl$_4$) : 3.54 (s, 3H) ; 2.23 (t, J = 6.5 Hz, 2H) ; 1.20-1.80 (m, 6H) IR (CCl$_4$) : 2925, 2855, 1735, 1440, 1355, 1190, 1170 cm^{-1} ^{13}C NMR:174.1 (s) ; 51.3 (q) ; 34.0 (t) ; 29.1 (t) ; 24.9 (t).

9 - Compound 2 was converted by a two step procedure : hydrolysis and hydrogenation, in 1,2-cyclooctanediol which was identical with an authentical sample of trans 1,2-cyclooctanediol prepared according to (10).

Diester 4 was hydrogenated and saponified to trans 1,2-cyclooctanedicarboxylic acid. That last reaction is known to give exclusively the trans diacid whichever cis or trans diester is used as starting material (11). On esterification that trans diacid gave back the trans diester which was identical with the hydrogenated form of diester 4.

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13- On purification by column chromatography on basic alumina compound 5 isome rise to 4-carbomethoxy-1,4 cyclooctadiene. ^{1}H NMR (60 MHz, CDCl$_3$) : 6.80 (t, 10 Hz, 1H) ; 5.47-5.90 (m, 2H) ; 3.73 (s, 3H) ; 3.20-1.00 (m, 8H). IR (neat) : 3005, 2925, 2840, 1705, 1640, 1455, 1430, 1275. ^{13}C NMR: 168.3 (s) ; 141.8 (d) ; 134.8 (d) ; 130.8 (d) ; 128.2 (d) ; 51.8 (q) ; 27.8 (t) ; 27.1 (t) ; 25.4 (t) ; 23.5 (t).

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(Received in France 14 November 1982)