Tetrahedron Letters No.50, pp. 6237-6240, 1966. Pergamon Press Ltd.
Printed in Great Britain.

COUPLING AND CYCLIZATION OF DIHALIDES USING NICKEL CARBONYL; A ONE-STEP SYNTHESIS OF 1,4,7-TRIMETHYLENECYCLONONANE FROM 1,1-BISCHLOROMETHYLETHYLENE

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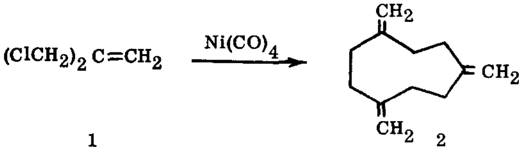
(Received 30 September 1966)

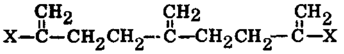
A previous note from this laboratory has described a new synthetic method for the formation of medium-sized carbocyclic rings containing unsaturation which depends upon the ability of nickel carbonyl to remove halogen from allylic 1,n-dihalides to form complexes of nickel whose further decomposition leads to cyclization. Thus, nickel carbonyl converts all *trans*-1,12-dibromo-3,10-dimethyldodeca-2,6,10-triene to a mixture of all *trans*- and *trans*,*trans*,*cis*-1,6-dimethylcyclododeca-1,5,9-triene (ratio 2 : 1) (1). This process can be regarded as an intramolecular version of the coupling of simple allylic halides discovered some years ago (2). We report here a particularly direct synthesis of a cyclononane derivative from a 4-carbon precursor, 1,1-bischloromethylethylene (1), and nickel carbonyl in a process which involves *both* intermolecular and intramolecular linking of carbon.

Reaction of 1,1-bischloromethylethylene (3-5) (1) (10 g.) with nickel carbonyl (56 g.) in 200 ml. of tetrahydrofuran under argon at 50° for 51 hr. led in 54% yield to a colorless hydrocarbon $C_{12}H_{18}$, found: C, 88.60; H, 11.16; Mol. Wt. 162 (mass spectrometry), which was identified as 1,4,7-trimethylenecyclononane (2) by a combination of physical and chemical data. The n.m.r. spectrum of the hydrocarbon exhibits only two peaks at 2.30 and 4.80 δ (δ=ppm. downfield shift from tetramethylsilane) in the ratio 2 : 1, and the infrared spectrum shows strong absorption at 6.07 and 11.15 μ attributable to $\rangle C{=}CH_2$. Catalytic hydrogenation afforded two isomeric hexahydro products (ratio *ca.* 4 : 1 by v.p.c.) whose n.m.r. spectra show methyl doublets typical of $-\underset{|}{C}H-CH_3$ units (0 82 and 0.86δ resp. with J=6.0 cps.) and no olefinic protons; found: Mol. Wt. 168 (mass spectrometry).



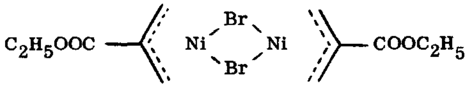
1 2

An independent synthesis of 2 was effected by the cyclization $(Ni(CO_4))$ in excellent yield of 1,9-dichloro-2,5,8-trimethylenenonane (3, $X{=}CH_2Cl$), which was prepared from the diester 3, $X{=}COOC_2H_5$ (found: Mol. Wt. 280.1681 by mass spectrometry), by reduction (AlH_3) (6) and halogenation ($SOCl_2$). The diester 3, $X{=}COOC_2H_5$, was produced from the reaction of 1,1-bischloromethylethylene with the π-complex 4 (7) in tetrahydrofuran.



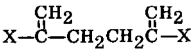
$$X{-}\overset{CH_2}{\overset{\|}{C}}{-}CH_2CH_2{-}\overset{CH_2}{\overset{\|}{C}}{-}CH_2CH_2{-}\overset{CH_2}{\overset{\|}{C}}{-}X$$

3



4

The cyclononane derivative 2 was also formed from a mixture of 1,1-bischloromethylethylene and 1,6-dichloro-2,5-dimethylenehexane 5 ($X{=}CH_2Cl$), and evidence was obtained for a process involving C_4-C_8 coupling and cyclization. Treatment of equimolar quantities of 1,1-bischloromethylethylene and 1,1,6,6-d_4-1,6-dichloro-2,5-dimethylenehexane (5, $X{=}CD_2Cl$) with nickel carbonyl in tetrahydrofuran produced a mixture of tetradeuterated and undeuterated 2, with about 88% of the C_{12} hydrocarbon 2 coming from the C_8-dichloride 5, $X{=}CD_2Cl$. The dichloride 5, $X{=}CH_2Cl$, was synthesized from the diester 5, $X{=}COOC_2H_5$ (found: Mol. Wt. 226.1204



$$X{-}\overset{CH_2}{\overset{\|}{C}}{-}CH_2CH_2\overset{CH_2}{\overset{\|}{C}}{-}X$$

5

by mass spectrometry), which in turn was made by coupling of ethyl α-bromomethylacrylate (8) induced by nickel carbonyl in tetrahydrofuran.

The reaction of 1 with nickel carbonyl was also carried out in tetraglyme to allow the detection of 1, 4-dimethylenecyclohexane, the product of cyclization at the stage of the C_8-dichloride 5, X=CH_2Cl, and it was found by vapor phase chromatography that this hydrocarbon was indeed produced as a minor product (*ca.* 11% yield). The use of nickel tricarbonyl triphenylphosphine as reagent in tetraglyme inhibited completely the formation of the C_{12} hydrocarbon 2 from 1 but had little effect on the yield of 1, 4-dimethylenecyclohexane. Further, although the reaction of the C_8-dichloride 5, X=CH_2Cl, with nickel carbonyl afforded mainly polymer and only *ca.* 10% yield of 1, 4-dimethylenecyclohexane, the use of nickel tricarbonyl triphenylphosphine as reagent with the C_8-dichloride increased the yield of this hydrocarbon to 60%. Thus, it appears that the presence of a single triphenylphosphine ligand on nickel favors ring closure at the C_8 stage relative to intermolecular coupling in this case.

The reaction of the C_4 dichloride 1 with nickel carbonyl in tetrahydrofuran also produces a ketonic product in *ca.* 5% yield which was identified as 3, 6-dimethylenecycloheptanone by physical and chemical data; found: Mol. Wt. 136. 0889 (mass spectrometry); calcd. for $C_9H_{12}O$: Mol. Wt. 136. 0888; n. m. r. spectrum: singlets at 2. 37δ (4H), 3. 06δ (4H), and 4. 92δ (4H); infrared absorption: 5. 81 μ (C=O) and 6. 07 and 11. 04 μ ($C=CH_2$). Treatment of this ketone with cold 1% sodium methoxide in methanol afforded 3, 6-dimethyl-2, 6-cycloheptadienone; ultraviolet max. (cyclohexane) 234 mμ (4. 00), sh. 262 mμ (3. 52); infrared absorption: 6. 00 and 6. 21 μ (sh. at 6. 05 and 6. 26 μ); n. m. r. singlets at 1. 94δ (6H, $2CH_3$), 2. 37δ (4H), and 5. 82δ (2H); found: Mol. Wt. 136. 0888 (mass spectrometry) (9).

A discussion of evidence relating to possible mechanisms for the linking of C_4 units and the subsequent cyclization to form the triene 2 will be reserved for a later time. With regard to the mechanism of coupling of simple allyl halides by nickel carbonyl, one particularly significant finding deserves mention. The binuclear π-allyl nickel (I) complexes of the type first made by E. O. Fischer, which are formed from allyl halide and nickel carbonyl (10), are obviously intermediates; however, we find that these complexes give rise to allylic coupling products not *by themselves* but only by further reaction with allyl halide (11).

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8. This ester was made from ethyl bisbromomethylacetate [T. Ferris, J. Org. Chem. 20, 780 (1955).] by reaction with 2, 6-lutidine.
9. For corresponding spectral data on 2, 6-cycloheptadienone itself, see E. W. Garbisch, Jr., J. Org. Chem. 30, 2109 (1965).
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11. This work was supported by N. S. F. Predoctoral Fellowships to M. F. S. (1964-6) and an N. S. F. research grant (GP 1955).