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METATHESIS REACTIONS BY IRIDIUM CATALYSTS: SYNTHESIS OF CIS-1,3-DIALKENYLCYCLOPENTANES

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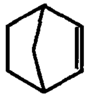
Although one of the widest scopes of the homogeneous metathesis of olefinic hydrocarbons involves the synthesis of difficulty accessible alkenes, only two reports concerning the molybdenum- or the tungsten-catalyzed synthesis of aliphatic dienes or trienes exist.[2,3] We now report the results of a synthetic and stereochemical study on the metathetical co-dimerization of norbornene 1 with aliphatic olefins, promoted by an iridium complex.

In the course of a current investigation on the catalytic activity of group VIII transition metal complexes in the metathesis reactions, we have observed that aliphatic olefins exert a marked influence on the metathetical polymerization of norbornene 1 promoted by di- μ-chloro-chlorobis(cyclooctene)iridium [4]. Using aliphatic olefin/1 molar ratios higher than 1, it is possible to isolate polymeric liquid products containing terminal groups corresponding to the alkylidene moieties of the aliphatic olefin, together with metathetical co-dimers of structure 2 in amounts strongly dependent on the type of aliphatic olefin used.



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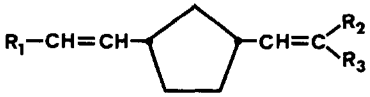

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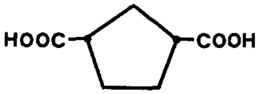
2a ($R_1=R_2=Me; R_3=H$) ; 2b ($R_1=Me; R_2=H; R_3=Et$)
2c ($R_1=R_3=Et; R_2=H$) ; 2d ($R_1=H; R_2=R_3=Me$)
2e ($R_1=R_2=H; R_3=n\text{-}Pr$); 2f ($R_1=R_2=R_3=Me$)



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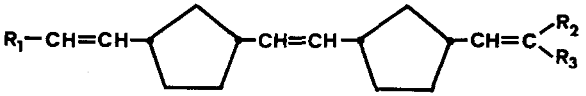

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The optimal conditions in order to keep the reaction at the co-dimer level in the highest yield when vinyl,vinylidene or internal olefins are used, are reported in Table 1.

The metathetical co-dimers, separated by fractional distillation from the reaction mixtures and purified by glc,were identified by elemental analysis, ir, nmr and mass spectroscopy. Their structure was confirmed by degradative oxidation to cis-cyclopentane-1,3-dicarboxylic acid 3.

Reference to Table 1 indicates that the reactivity of the various aliphatic olefins employed is rather diversified. Thus, the order of reactivity is 2-pentene≃2-butene>isobutene> 1-pentene≫2-methyl-2-butene. In particular, the best results are obtained using internal disubstituted olefins. On the contrary, ethylene does not react with 1 and inhibits the polymerization of this monomer also when ethylene/1 low molar ratios are employed. In accord with this result, $[IrCl(C_2H_4)_2]_2$ and $[IrCl(C_2H_4)_4]$ were found to be poor catalysts for polymerization of 1. Worth of mention is that the cross-reaction of 1 with isobutene represents, to our knowledge, the first example of a successful homogeneous metathesis involving a vinylidene olefin. Metathetical products of structure 4, in amounts comparable to those of the corresponding co-dimers 2, are formed in the reaction of 1 with disubstituted vinylidene, or vinyl olefins. However, only one of these telomers that one deriving from the reaction of 1 with 2-butene, has been fully characterized.

As previously noted[4], di-μ-chloro-chlorobis(cyclooctene)iridium which does not display catalytic activity for disproportionation of aliphatic olefins, is transformed under the action of 1 into a species that exhibits some activity for metathesis of such compounds. In fact, in the reaction of 1 with 2-pentene are formed the three co-dimers 2a, 2b, and 2c which may derive from metathesis of 1 with 2-butene, 2-pentene, and 3-hexene, respectively, or from metathesis of 2b with 2-pentene. The molar ratio of 2a, 2b, and 2c is essentially 1:2:1. Significant amounts of free 2-butene and 3-hexene are also present in the reaction mixture. Analogously, small amounts of ethylene and 4-octene are formed in the co-reaction of 1 with 1-pentene. Due to the inhibiting action of ethylene, the presence of this olefin in the reaction mixture justifies the low yield of 2e.

The results in Table 1 also indicate that 2e is contamined with a large amount of an isomeric compound. This may be due to the isomerization activity toward vinyl olefins of di-μ-chloro-chlorobis(cyclooctene)iridium[5] or of a species derived from it.

The stereochemistry of compounds 2a, 2b, 2c, and 2e reveals that the iridium catalyst does not exhibit stereoselectivity, at least under our experimental conditions. In fact, each of dienes 2a, 2b, and 2c is constituted of three stereoisomers which, on the basis of ir analysis, we believe to be the three geometrical isomers (E) (Z), (E) (E), and (Z) (Z). Analogously, 2e exists in two geometrical isomers. Significantly, the ratio among these stereoisomers is independent of the (E)/(Z) distribution of the initial aliphatic olefin.

In order to compare the results of these iridium-catalyzed reactions with those of the corresponding tungsten-catalyzed reactions, we have performed the cross-metathesis of 1 with 1-pentene and 2-pentene in the presence of the WCl_6-$SnMe_4$ system. This catalyst has been proved to be of optimum activity and selectivity for disproportionation of aliphatic olefins and unsaturated fatty acid esters[6]. The experimental conditions were: $SnMe_4/WCl_6$ molar ratio = 1.2; $1/WCl_6$ molar ratio = 60; aliphatic olefin/1 molar ratio = 2.0; C_6H_5Cl solvent/aliphatic olefin volume ratio = 2-3; reactions at room temperature for 48-60 hr. Glc analysis of the reaction

Table 1

Metathetical co-dimerization of norbornene (Nb) with aliphatic olefins promoted by $[(\text{cyclooctene})_2\text{IrCl}]_2$ [a)]

Run	Nb (mol)	Alkene	$\frac{\text{Alkene}}{\text{Nb}}$ (mol ratio)	$\frac{\text{Nb}}{\text{Ir complex}}$ (mol ratio)	Reaction time (hr)	Co-dimer Structure	Yield [b)] (mol %)
1	0.127	(Z)-2-butene	2.0	1300	120	2a	11
2	0.127	isobutene	2.0	1300	120	2d [c)]	5
3	0.159	(Z)-2-pentene	2.1	600	56	2a+2b+2c [d)]	12
4	0.105	(E)/(Z)-2-pentene	2.1	1000	56	2a+2b+2c [d)]	11
5	0.319	1-pentene	2.0	600	120	2e [e)]	2 [e)]
6	0.055	2-methyl-2-butene	100.0	600	140	2f [f)]	trace [f)]
7	0.106	ethylene	0.5	600	140	-	-

a) Reactions carried out at room temperature without solvents except for the runs 1, 2, and 7 in which 15 ml of pentane were used. Each run has been repeated at least thrice.

b) Based upon norbornene introduced.

c) The reaction mixture contains ca. 95% of 2d and 5% of an isomeric compound.

d) The molar ratio of 2a, 2b, and 2c is essentially 1:2:1.

e) This co-dimer is contamined with 56% of an isomeric compound.

f) The co-dimer could not be isolated, but the presence was revealed by glc. The principal reaction product is a methanol insoluble semi-liquid polymer (36% yield) containing $CH_3CH=$ and $(CH_3)_2C=$ terminal groups.

mixtures has shown that for the cross-metathesis of 1 with 2-pentene the yield of 2a, 2b, and 2c (in 1:2:1 molar ratio, respectively) is 6%, namely half of that obtained in the corresponding iridium-catalyzed reaction. On the other hand, the yield of 2e for tungsten-catalyzed reaction of 1 with 1-pentene is 3%, and unlike what observed in the reaction promoted by di- μ-chlorochlorobis(cyclooctene)iridium, 2e is isomerically pure.

In summary, diolefins of general formula 2 (some of which may be of importance in macromolecular chemistry) are conveniently prepared by iridium-catalized cross-metathesis of norbornene with aliphatic olefins when vinylidene or internal disubstituted olefins are involved. The analogous cross-metathesis catalyzed by $WCl_6/SnMe_4$ gives lower yields. However, either the iridium or the tungsten-catalyzed reactions, at least under our experimental conditions, appear to be of poor synthetic value when vinyl olefins are used as co-reactants.

The possibility of using iridium-catalyzed reactions for the metathetical co-dimerization of norbornene and other ring-strained cycloolefins with internal alkenes carrying a functional group is being studied.

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References

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2. E.A.Zuech, W.B.Hughes, D.H.Kubick, E.T.Kittleman, J.Amer.Chem.Soc., 92, 528 (1970).
3. C.Pinazzi, C.R.Acad.Sci. Ser.C, 276, 1077 (1973).
4. L.Porri, R.Rossi, P.Diversi, A.Lucherini, 164° Meating of American Chemical Society, Polymer Preprints, 13, 897 (1972).
5. H. van Gaal, H.G.A.M.Cuppers, A.van der Ent, Chem.Comm., 1694 (1970).
6. P.B.van Dam, M.C.Mittelmeijer, C.Boelhouwer, J.C.S.Chem.Comm., 1221 (1972).