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CATALYTIC TETRAMETHYLALLENE/BUTADIENE COOLIGOMERIZATION

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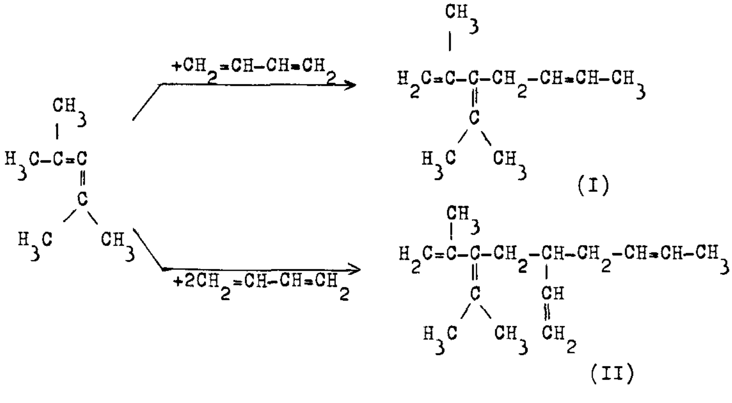
Some iron-catalyzed cooligomerizations between dienes (conjugated dienes, norbornadiene) and other unsaturated hydrocarbons (ethylene, α-olefins, acetylenes) were previously described by us (1, 2). Now we report the tetramethylallene (TMA)/butadiene (BD) cooligomerization in the presence of the same catalysts. The Ziegler-Natta systems $FeCl_3$/ /i-C_3H_7MgCl in diethylether and Fe-triacetylacetonate/$Al(C_2H_5)_3$ in benzene as well as the bis(cyclooctatetraene) iron(0) in benzene are suitable catalysts. The cooligomers predominantly consist of 1:1 and 1:2 adducts (30-50 % of the introduced TMA).

The 1:1 adducts consist of five different C_{11} isomers. One of the two principal ones is formed according to scheme I. The 1:2 adducts (C_{15} isomers) almost exclusively consist of compound II.



In both cases the addition involves a hydrogen transfer from a methyl group of TMA to a BD unit. Unlike in all other codimerizations involving hydrogen transfer, catalyzed by organometallic systems containing an VIII group transition metal, the carbon atom that loses the hydrogen does not form a new C-C bond with the comonomer unit.

Although, as known, TMA easily isomerizes to the conjugated 2,4-dimethyl-1,3-pentadiene (DPD) (3), formation of I and II does not proceed over a previous isomerization of this type. Actually, the same cooligomers could not be found in the reaction of TMA with

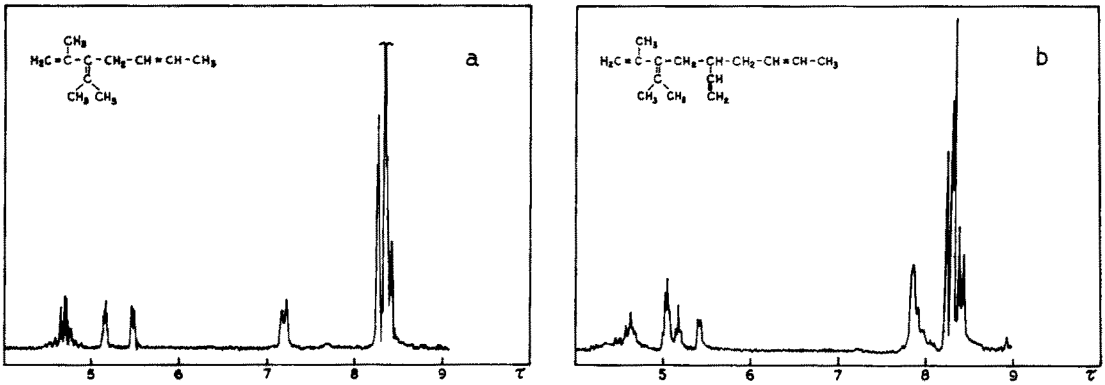


Fig. 1 - ^{1}H nmr spectra of I and II
(Varian 100 Mc, CCl_4, TMS)

BD under the same conditions. Moreover, even if the same iron catalysts proved to be capable of isomerizing TMA to DPD, no appreciable amounts of DPD have been found in the reaction products of the TMA/BD cooligomerization. The hydrogen abstraction from a methyl group by the action of iron compounds has been reported (4).

The present reaction may be interpreted as occurring over an oxidative addition of the allenic unit to the iron, analogous to that recently proposed by us for other iron-catalyzed oligomerizations involving hydrogen transfer (5).

Structural Assignment

Three and four moles of H_2 were absorbed in the Pd/charcoal catalyzed hydrogenation at room temperature of I and II respectively. The ozonization of I (in $CHCl_3$ at -30°C) followed by H_2O_2/acetic acid cleavage and methylation with CH_2N_2 gave good yields of dimethylmalonate (identified by glc), whereas II did not give the expected propane-1,2,3-tricarboxylate: the presence of the tertiary carbon atom likely causes a more severe demolition. The oxidation of I with KJO_4 and $KMnO_4$ (6) yielded acetone.

The mass spectrum of I showed a 150, that of II a 204 parent peak. The latter showed also 149 (loss C_4H_7) and 109 (loss C_8H_{11}) peaks.

The ir spectrum of I showed absorptions at 1392, 760 (cis double bond), 888 (vinylidene group), 1625 (both unsaturated groups), and 1364 cm^{-1} (methyl group). That of II shows absorptions at 1400, 705 (cis double bond), 988, 905 (vinyl group), 890 (vinylidene group), 1629, 1635 (the above double bonds), and 1368 cm^{-1} (methyl group).

The ^{1}H nmr spectra of I and II are given in figure 1. That of I shows a 4/14 olefinic/aliphatic protons ratio. The signals are centered at 4.70 (2H, cis $-C\underline{H}=C\underline{H}-$), 5.15 + 5.45 (1+1H, $>C=C\underline{H}_2$), 7.20 (2H, $-C=C-C\underline{H}_2$), and 8.25–8.40 τ (12H, $-C\underline{H}_3$). That of II shows a ~ 7/17 olefinic/aliphatic protons ratio. The signals are centered at 4.70 (3H, cis-$C\underline{H}=C\underline{H}-$ + $-\underline{H}C=CH_2$), 5.04 (2H, $-HC=C\underline{H}_2$), 5.18 + 5.42 (1+1H, $>C=C\underline{H}_2$), 7.85 (5H, $-C=C-C\underline{H}_2-$ + $-C=C-\overset{\diagup}{\underset{\diagdown}{C}}\underline{H}$), 8.20–8.40 τ (12H, $-C\underline{H}_3$).

The uv spectra of I and II show a shoulder of ~ 230 nm (ε = about 2000), instead of the expected maximum due to the two conjugated double bonds. This may be attributed to a conformationally originated lack of conjugation.

Typical TMA/BD Cooligomerization

An evacuated 100 ml stainless steel autoclave, cooled to −80°C, was charged in the order with 15 ml BD, 20 ml TMA, 20 ml diethylether, 1 ml n-octane (internal standard), 7 ml of a 2.5 M $i-C_3H_7MgCl$ Grignard solution in diethylether, 5 ml of a diethylether solution of $FeCl_3$ (400 mg). The stirred reactor was kept for 48 hrs at 50°C. The crude reaction product was analyzed by glc (programmed 50–250°C, silicon rubber, He). 7.68 g of 5 different C_{11} products (1:1 adducts) were found, I covering almost 50% of them. The other isomers could not be isolated so far. Moreover, 4.10 g of C_{15} products (1:2 adducts), consisting almost exclusively of compound II, were obtained. I and II were separated by preparative g l c (programmed 175–250°C, apiezon, He); purity $\geqslant$ 97 %.

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