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EVIDENCE FOR ANCHIMERIC ASSISTANCE BY THE Cp_2ZrCl-GROUP IN THE HOMOLYTIC CLEAVAGE OF AN $O-CH_3$ BOND

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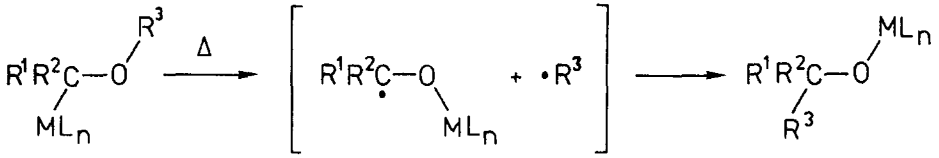
Summary: Anchimeric assistance by a transition metal in the homolysis of a C-O bond is discussed for the thermal rearrangement of methyl(zirconocenyldiphenylmethyl)ether 1c.

Neighboring-group participation, a common feature in carbonium ion chemistry, is a quite rare event in radical forming processes. In this respect certain organometallic neighboring groups seem to play an exceptional role. A prominent series of examples of the trimethylsilyl group assisting the homolytical cleavage of C-O bonds in alkyl(silylmethyl)ethers (1a) has recently been described.[1)] Exceptionally low activation barriers were observed for the thermally induced rearrangement to siloxycompounds 3a in cases where both radical fragments formed were sufficiently stabilized. We have examined the thermolysis of the related α-substituted ether 1c. It seems that the analogous radical reaction path can be observed at considerably reduced temperatures compared to the silicon systems even for R^3=methyl using the suitable transition metal center (here: zirconium) as a neighboring group.



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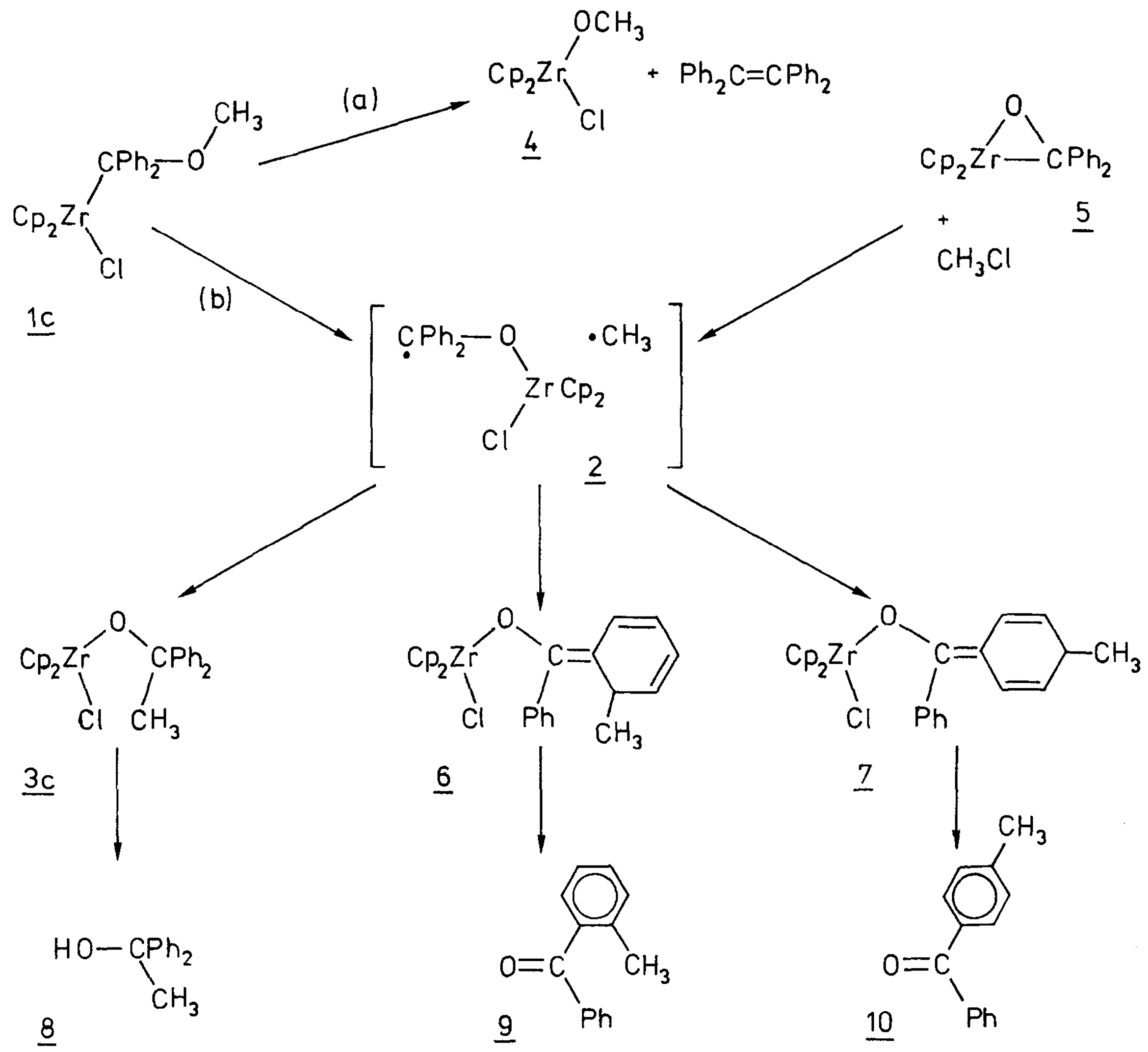
1a: ML_n = $SiMe_3$, R^1 = R^2 = Ph, R^3 = Benzyl, T = 185°C[1)]
1b: ML_n = $SiMe_3$, R^1 = R^2 = Ph, R^3 = Methyl, no reaction below $T_{decomp.}$ = 240°C[1)]
1c: ML_n = Cp_2ZrCl, R^1 = R^2 = Ph, R^3 = Methyl, T = 100°C

The α-zirconocenylether 1c was prepared treating Cp_2ZrCl_2 with α-lithiated benzhydrylmethylether in diethylether solvent. It was taken care that the temperature was kept below -20°C to avoid Wittig rearrangement of the educt. Pure 1c was obtained after recrystallization from chloroform [10% isolated yield, yellow crystalls, Fp = 153°C, ^{1}H NMR ($CDCl_3$, rel. TMS): δ 7.2 (br.m. 10H), 5.78 (s, 10H), 4.13 (s, 3H), UV: λ_{max} = 287 nm, ε = 26000, analysis, C, H found: 63.49, 5.29 (calculated: 63.48, 5.11)]. The absence of minor amounts of by-products which would interfere with the analysis of the expected product mixture (see below) was ensured by carefully examining the hydrolysis mixture of 1c. By comparative experiments we made sure that 0.5% of each of the compounds 8, 9 and 10 would have been detected by the method of analysis (GLC; GLC/MS) applied for minor components.

The thermally induced rearrangement of 1c can be observed at remarkably low temperatures. A slow reaction (a) at ambient temperature ($\tau_{1/2}$ ≈ 48 hrs.) yields two products identified as $Cp_2Zr(OCH_3)Cl$ (4) and tetraphenylethylene by comparison with authentic material. Raising the temperature one observes increasing amounts of products from a different reaction path (b). This reaction results in a mixture of three organometallic compounds. By comparison with an independently synthezised sample the major component of this mixture was identified as the zirconoxycompound 3c. The two accompanying minor components are formed in amounts that do not allow a safe characterization by the usual combination of spectroscopic methods. Therefore the product mixture was hydrolyzed. After treatment with oxygen or iodine three compounds 1.1-diphenylethanol 8, 2-methylbenzophenone 9, and 4-methylbenzophenone 10 were obtained in a ratio of 87:8:5 besides products derived from reaction path (a). From the observation of 9 and 10 we deduce the formation of their organometallic precursors 6 and 7 as products formed by path (b). Within the limits of our analysis the ratio of the three rearrangement products appears to be independent of the reaction temperature. The thermolysis of 1c was carried out in different solvents. The rate of disappearance of the starting material 1c at 100°C varies only by factor 2 substituting toluene by 1.2-dichloroethane. Increasing solvent polarity seems to cause a slight increase in the (a)/(b) ratio (100°C: toluene 60/40, tetrahydrofuran 70/30, 1.2-dichloroethane 77/23). A practically identical 8 : 9 : 10 ratio was found in these solvents.

It has been shown that radical pairs formed from ketyl and methyl or primary alkyl radicals may predominantly react via geminate radical recombination within the solvent cage$^{2)}$. This causes a principal problem unveiling the presence of radical processes since the commonly employed probes (as used for 1a: EPR, trapping and crossover experiments) depending on free radicals escaped from the cage can no longer be applied for systems like 1c. Fortunately, however, the intermediacy of radical pairs often can be detected by the intramolecular formation of additional compounds besides the expected 'normal' rearrangement products.



The fact that the ring-substituted benzophenones 9 and 10 are among the reaction products is a strong indication of a radical process operating in the thermolysis of 1c. The appearance of these products in a variety of quite different processes (e.g.: Wittig rearrangement,2) Grignard addition to diarylketones,3) reaction of alkali metal ketyls with alkyl halides2)) has been interpreted as being typical for the intermediacy of type 2 radical pairs. Following this interpretation the product ratio observed in our case appears to be characteristic for dominating product formation from 2 via geminate radical recombination. Moreover, the identical organometallic product mixture recently was obtained independently by treatment of the η^2-benzophenone zirconocene complex 5 with methyl halide, a reaction almost certainly passing through an intermediate radical pair 2. 4) We found no evidence for another than the product determining intermediate 2 being formed in the rate determining step (b). Especially the possible formation of 2 via polar intermediates (as has been discussed in detail for the silicon system 1a 1)) either formed directly from 1c or in a side reaction at some stage of the α-elimination reaction (a) seems unlikely in view of the observed temperature dependence of the (a)/(b)ratio and the negligible solvent dependence of product-ratio as well as reaction rate observed in the thermolysis of 1c. 5)

Our observations thus suggest that the low activation barrier of the C-O bond cleavage observed for 1c in contrast to simple alkyl ethers 6) might be interpreted as a consequence of a pronounced neighboring-group participation by the transition metal center in a homolytic bond breaking process. For the realization of anchimeric assistance in radical processes certain thermodynamic requirements undoubtedly have to be met. 1) Quite remarkable, however, is the obviously much faster reaction of the zirconocenylether 1c compared to its silicon analog despite their accidental similarities of relevant thermodynamic parameters. For the present example, where the magnitude of the activation barrier - as expected for a quite unsymmetrical reaction profile - predominantly seems to be determined by the developing interaction between metal and the ether oxygen but less by the energy content of the radical to be formed, energetics and geometrical features of the acceptor orbital on the metal center 7) appear to be important additional controlling factors.

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