Transition-metal-catalysed Reactions of Diazoesters. Insertion into C–H Bonds of Paraffins by Carbenoids

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Summary Rhodium(II) carboxylates of perfluoroacids are very efficient catalysts for promoting the insertion of carbenes (carbenoids) (generated from diazoesters) into the C–H bonds of alkanes with selectivities which differ from those observed in typical free-carbene processes.

WE have already shown the beneficial influence of strongly electron-withdrawing carboxylate ligands on some Rh^{II}-catalysed carbene reactions (*e.g.* addition to aromatic molecules[1]). We report herein the efficiency of rhodium(II) derivatives of strong organic acids ($pK_a < 1$) for promoting, under mild conditions, the insertion of carbenes (carbenoids) generated from diazoesters (Alk–DA) into the C–H bonds of alkanes.

TABLE 1. Yields of C–H monoinsertion products in the $Rh–CF_3$-catalysed decomposition of EtDA in alkanes.[a]

Alkane	Insertion yield/%[b]	Alkane	Insertion yield/%[b]
$c\text{-}C_5H_{10}$	50 (68[c])	$n\text{-}C_5H_{12}$	65 (92[c])
$c\text{-}C_6H_{12}$	78 (90[c])	$n\text{-}C_4H_8Me_2\text{-}2,3$[g]	46 (88,12[e])
$c\text{-}C_6H_{11}Me$	29[d]	$n\text{-}C_4H_9Me\text{-}2$[h]	71 (5,25,66,4[f])
$c\text{-}C_7H_{14}$	43 (62[c])	$n\text{-}C_5H_{11}Me\text{-}2$[i]	68[d]
$c\text{-}C_8H_{16}$	64		

[a] Reaction conditions: 22 °C, 100 mmol of cycloalkane or 200 mmol of n-alkane, 3 mmol of EtDA, $2{\cdot}0$—$2{\cdot}2 \times 10^{-3}$ mmol of $Rh–CF_3$. Yields were based on EtDA (g.l.c.); addition time 4 h with an automatic syringe. [b] Average of at least two runs. [c] Optimized yields at the alkane boiling point. [d] Mixture of isomers. [e] C–H insertion (%) at C-1 and C-2, respectively. [f] C–H insertion (%) at C-1, C-2, C-3, and C-4, respectively. [g] 2,3-Dimethylbutane. [h] 2-Methylbutane. [i] 2-Methylpentane.

Table 1 summarizes the results obtained with some (cyclo)alkanes and tetrakis(trifluoroacetato)dirhodium(II) (rhodium trifluoroacetate, $Rh–CF_3$) as the catalyst.†

The yields were good[2] and vary *inter alia* with the reaction temperature (see Table 1 for the effect at the alkane boiling point) and the ratio of substrate to diazoester. When the latter was low ($<$*ca.* 20—30), the formation of oligomers of carbene predominated, with fast catalyst deactivation. Although insertion into C–H bonds by carbenoids is an uncommon process,[3] several observations indicate that free carbenes are not the active species. Firstly, the Rh^{II}-catalysed C–H insertions into n-pentane exhibit regioselectivities significantly different from those observed in typical free-carbene processes. Indeed, C–H insertions at C-1, C-2, and C-3 of n-pentane were respectively 7, 66, and 27% (catalytic reaction conditions of Table 1), as compared with 38, 45, and 25% when the carbene was photochemically promoted, *i.e.* catalytic insertion into primary C–H bonds was nearly suppressed. Secondly, competitive experiments between pairs of alkanes showed that, with $Rh–CF_3$ as the catalyst, the high-molecular weight (long-chain) alkane was preferred {*e.g.* ratio of inserted n-pentane to n-decane 0·5 [equivalent weights, with ethyl diazoacetate (EtDA)]}. A similar trend was also observed with the cycloalkanes and the results are summarized in Table 2.

Moreover, the selectivity of insertion strongly depended on both the diazoester alkoxy-group and the metal counter-ion. For example, when the diazoester was catalytically decomposed by $Rh–CF_3$ in a mixture of cyclopentane and cyclo-octane (equivalent weights) the relative ratio of in-

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† All the compounds described in this work were identified by g.l.c. (including analysis on capillary columns, 50 m × 0·25 mm, FFAP), by comparison with authentic samples synthesized by independent methods, and by coupled g.l.c.–m.s. When needed, corrections were made for the relative responses to the catharometer.

Table 2. Selectivities of C–H insertions in intermolecular competitions.[a]

Diazoester	Method of decomposition[b]	Ratio of C–H insertion between cycloalkanes C_5/C_8	C_6/C_8	C_6/C_5
MeDA	A, RhCF_3	0·13	0·3	1·5
MeDA + EtDA	B and C	*ca.* 1·0	1·0	1·0
EtDA	A, RhCF_3	0·6	0·75	1·3
EtDA	A, RhC_7F_{15}	1·8	1·35	

[a] Catalytic reaction conditions were the same as in Table 1. The relative insertions (%) are corrected for the number of hydrogen atoms. [b] A, catalyst; B, photochemical, 300 W high-pressure Hg lamp, water-cooled Pyrex jacket; C, thermal, sealed ampoules, 150 °C (for photochemically promoted C–H insertions, see also H. Tomioka, M. Itoh, S. Yamakawa, Y. Isawa, *J. Chem. Soc., Perkin Trans. 2*, 1980, 603).

serted cyclopentane to cyclo-octane was 0·13 with MeDA and 0·6 with EtDA. However, replacement of Rh–CF_3 by Rh^{II} perfluoro-octanoate (Rh–C_7F_{15}) promoted a dramatic reversal of selectivity, the ratio changing to 1·8.

Preferential complex solvation by one of the alkanes could account for the surprising selectivities observed in competitive experiments. The alterations in the relative selectivities brought about in competition experiments by a simple homologation of the diazoester alkoxy-group are unique and are indicative of the importance of carbenoid–substrate lipophilic interactions,‡ a finding which is substantiated by the sensitivity of the reaction to alkane substitution (*e.g.* competition between methylcyclohexane and cyclohexane with EtDA and Rh–CF_3 gave a C–H insertion ratio of 0·7; competition between n-pentane and 2,3-dimethylbutane gave a C–H insertion ratio of 1·45).

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‡ The influence of the diazoester alkoxy-group was previously evidenced in carbene cycloadditions to olefins, see A. J. Hubert, A. F. Noels, A. J. Anciaux, and Ph. Teyssié, *Synthesis*, 1976, 600; *J. Org. Chem.*, 1980, **45**, 695.

[1] A. J. Anciaux, A. Demonceau, A. J. Hubert, A. F. Noels, and Ph. Teyssié, *J. Chem. Soc., Chem. Commun.*, 1980, 765; *J. Org. Chem.*, 1981, **46**, 873.

[2] For a comparison with copper catalysts, see L. T. Scott and G. J. Decicco, *J. Am. Chem. Soc.*, 1974, **96**, 322.

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