Catalytic Control of Reactions of Dipoles and Carbenes;[1] an Easy and Efficient Synthesis of Cycloheptatrienes from Aromatic Compounds by an Extension of Buchner's Reaction

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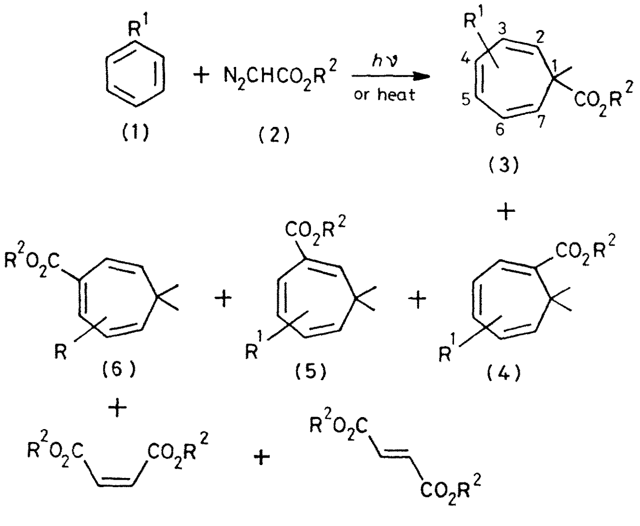
Summary Rhodium salts from strong carboxylic acids [particularly rhodium(II) trifluoroacetate] are novel and highly efficient catalysts for the preparation of substituted cycloheptatriene carboxylates from aromatic hydrocarbons and diazo-esters, and in contrast with the classical Buchner procedures these rhodium catalysts lead specifically to the 1-isomer (**3**), avoiding its subsequent prototropic conversion into conjugated isomers.

Since Buchner's classical work, the formation of cycloheptatrienes by cycloaddition of carbenes to aromatic substrates has been thoroughly investigated owing to its great mechanistic[2] and also preparative interest (particularly in the field of natural products).[3] Hitherto, however, finding selective, efficient processes for the direct preparation of substituted cycloheptatrienes from carbenes (*i.e.* generated by decomposition of diazo-compounds) has been a problem, the reaction yielding in all cases complex mixtures of products which are very difficult to separate (see the Scheme).

We now report that rhodium(II) carboxylates of strong organic acids are highly efficient in promoting the addition



Scheme

of carbenes to aromatic substrates, permitting ready and sometimes regioselective access to substituted cycloheptatrienes For example, tetrakis(trifluoroacetato)-dirhodium(II) (rhodium trifluoroacetate) catalyses the formation of the non-conjugated cycloheptatriene (**3**) from the diazo-esters (**2**) with an unexpectedly high selectivity The yield, generally good, is practically quantitative in the case of benzene and toluene (Table) Moreover, with substituted benzenes, (**1**, R ≠ H) the distribution of isomers reveals that the attack, in several cases, is remarkably regioselective (Table)

In a typical preparation of cycloheptatriene-1-carboxylates, the diazo-ester (5 mmol) was continuously added, within 2 h, with a motor-driven syringe (Sage, model 352), to the solution containing the catalyst (2—4 × 10^{-2} mmol) in the aromatic substrate (0 1 mol), at room temperature with magnetic stirring The product was analysed by g l c using an internal standard In preparative experiments, the product was distilled *in vacuo* after evaporation of the solvent The cycloheptatriene fractions were identified by comparison with reported data where possible and by the usual spectroscopic methods (i r , mass, n m r), all compounds yielding satisfactory elemental analysis

It should be emphasized that it is the kinetic isomer that is selectively produced (arising from sigmatropic hydrogen-shifts) and not the thermodynamic one Thus naphthalene yields the corresponding norcaradiene-intermediate addition product (instead of the final cycloheptatriene) in good yield up to 85% with rhodium(II) methoxyacetate as catalyst and butyl diazoacetate It is also noteworthy that the efficiency of the catalysts is strongly dependent on the electron-withdrawing ability of the carboxylate ligand, *e g* , for benzene acid, pK_a (% yield) CF_3CO_2H, 0 23 (100%), $C_6F_5CO_2H$, 1 48 (89%), $MeOCH_2CO_2H$ 3 57 (30%), $MeCO_2H$, 4 76 (7%), Bu^tCO_2H, 5 03 (5%) This is another example of the important role played by these halogenocarboxylate ligands in co-ordination chemistry [4]

Table Formation of the methyl cyclohepta 2 4 6 triene carboxylates (**3**) from (**1**) (100 mmol) methyl diazoacetate (5 mmol) and rhodium(II) trifluoroacetate (0 02 mmol) at 22 °C

Substrate (**1**)	Yield	Distribution of isomers of (**3**)[a]					
Benzene	100		(100)				
Toluene	95	4	(56)	3	(23)	2	(17)
o Xylene	80	2 3	(43)	3 4	(39)	4 5	(18)
m Xylene	90	2 4	(12)	2 6	(43)	3 5	(43)
p Xylene	90	2 5	(85)	3 6	(10)		
Anisole	73	3	(8)	4	(56)		
Chlorobenzene	72	4	(80)	3	(15)	2	(5)
Fluorobenzene	46	4	(80)	3	(12)	2	(8)
Pyridine	0	Strongly inhibiting ligand					

[a] The first number refers to the position of the substituents relative to the carboxylate group numbers in parentheses are the proportions (mole %) of the corresponding isomer present in the mixture of the carboxylates (**3**) mixture The balance to 100% is made up of unidentified isomers

In contrast with the observation that for olefin cyclo propanation with rhodium(II) carboxylates lipophilic non-bonded interactions determined the reactivity [1] the present results clearly indicate that for carbene addition to aromatic molecules it is electronic factors which control the reactivity of the rhodium carbenoid

In conclusion these systems besides their interest in offering a new approach to a better mechanistic understanding of the behaviour of carbenoids are of great preparative value and are quite versatile in their applications, *e g* polystyrene is easily carboxylated in solution [5]

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[1] For Part 1 and references to related publications see A J Anciaux A J Hubert A F Noels N Petiniot and Ph Teyssie *J Org Chem* , 1980, **45** 695 N Petiniot A J Anciaux A F Noels A J Hubert and Ph Teyssie *Tetrahedron Lett* 1978 1239

[2] For general references on Buchner synthesis and diazo ester reactions see V Dave and E W Warnhoff *Org React* 1970, **18** 217 D S Wulfman, G Linstrumelle and C F Cooper Synthetic Application of Diazoalkanes Diazocyclopentadienes and Diazo azacyclopentadienes Vol II, ed S Patai Wiley–Interscience New York 1978 ch 18 D S Wulfman and B Poling, Reactive Intermediates, Vol **1**, ed R A Albramovitch, Plenum Press, London - New York, 1980, ch 5

[3] D Lloyd, 'Carboxylic Non benzenoid Aromatic Compounds Elsevier Amsterdam 1966 pp 122 and 125

[4] See also the striking influence of the trifluoroacetate ion in Ni catalysed polymerisation of butadiene Ph Teyssie, A Devaux, P Hadijandreou, M Julemont, J M Thomassin, E Walckiers, and R Warin, Preparation and Properties of Stereoregular Polymers eds R W Lenz and F Ciardelli, Reidel Dordrecht 1980, p 131

[5] A J Hubert, A F Noels, and Ph Teyssie, unpublished results