

TRANSITION-METAL-CATALYSED REACTIONS OF DIAZOESTERS : SYNTHESIS OF CHRYSANTHEMIC AND PERMETHRIC ACID ESTERS BY CYCLOPROPANATION OF CONJUGATED DIENES^x

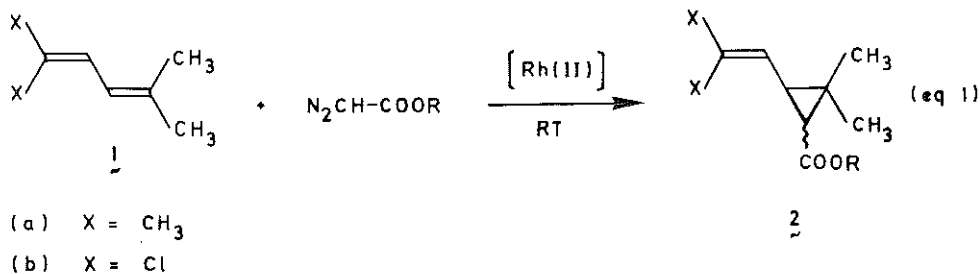
A. Demonceau, A.F. Noels,^x A.J. Anciaux, A.J. Hubert⁽⁺⁾ and P. Teyssié
 Laboratory of Macromolecular Chemistry and Organic Catalysis,
⁽⁺⁾Laboratory of Organic Synthesis and Catalysis,
 University of Liège, B-4000 Sart-Tilman, Belgium

Received : 06/09/1984 - Accepted : 17/09/1984

ABSTRACT

Pyrethroid precursors (permethric and chrysanthemic acid esters) are efficiently synthesized by rhodium(II)-catalysed cyclopropanation of the properly substituted conjugated diene. Reaction selectivities depend on both the catalyst counter-ion and the diazoester alkoxy-group (carbene precursor) and are attributed to non-bonded interactions.

Pyrethroids derived from chrysanthemic acid 2-a (R=H) and permethric acid 2-b (R=H) exhibit exceptionally potent insecticidal activity together with very low mammalian toxicity and rapid biodegradability.¹ Therefore, their synthesis from readily available precursors provides an attractive commercial target.²



The synthetic goal can be met by direct cyclopropanation of dienes **1** with diazoesters under homogeneous conditions. Traditionally, such reactions have been promoted by copper derivatives,³ catalysts which are however not very efficient in this particular case. Recent works indicate that a number of reactions where a carbene (generated from a diazoester) is transferred onto an olefinic bond, presumably via formation of a metal-carbene complex (carbenoid), can be efficiently controlled by catalytic amounts of rhodium(II) carboxylates, Rh₂(O₂C-R')₄ (by convention Rh-R').⁴ It was shown that in such reactions, the carboxylate counter-ion R' plays an important role. According to its electronic, steric and/or lipophilic requirements, it largely determines the efficiency and selectivity of carbenoid intermediate (regio- and stereo-selectivities).⁴

^x This paper is dedicated to Professor R.H. Martin for his 70th birthday.

Those features are again evidenced in the Rh(II)-catalysed cyclopropanation of 2,5-dimethyl-2,4-hexadiene (1-a) and of 1,1-dichloro-4-methyl-1,3-pentadiene (1-b). While 1-a gives a quantitative yield of 2-a ($Z:E$ ratio = 0.7) with any rhodium carboxylate tried, the yield drops to less than sixty per cent with 1-b , addition taking place exclusively on the 3,4-double bond, a further illustration of the electrophilic nature of rhodium carbenoids. Although with Rh-CH_3 as catalyst, the yields are not much influenced by a change of the diazoester alkoxy-group, the ratio of Z to E isomers is to some extent. Such an effect is much more clearcut with other Rh(II) derivatives. The strong influence of the diazoester on the stereochemical outcome of the reaction is exemplified in Table 1: by using $n\text{-Bu}$ diazoacetate and Rh(II) m -(trifluoromethyl) benzoate ($\text{Rh-C}_7\text{H}_4\text{F}_3$) as catalyst, the yield of 2-b goes up to 96%, together with a Z to E ratio of 1.53. Quite generally, the bulkier the alkyl-group of the diazoester, the higher the $Z:E$ ratio of the products.

TABLE 1

Rhodium(II) carboxylate-catalysed cyclopropanation of 2,5-dimethyl-2,4-hexadiene (1-a) and 1,1-dichloro-4-methyl-1,3-pentadiene (1-b).

Rh(II) carboxylate Rh-R'	Alkyl diazoacetate (RDA)	Yield (%) in cyclopropanes 2-a (Z/E ratio)	Yield (%) in cyclopropanes 2-b (Z/E ratio)
Rh-CH ₃	MeDA	100 (0.64)	56 (0.93)
	EtDA	100 (0.69)	54 (1.00)
	<i>n</i> -BuDA	100 (0.75)	58 (1.18)
	<i>t</i> -BuDA	100 (0.56)	56 (1.29)
Rh-CF ₃	EtDA	85 (0.67)	29 (0.93)
Rh-C ₆ HCl ₂ N ₂ O ₄ ^a	EtDA	53 (0.77)	15 (1.14)
	<i>t</i> -BuDA		15 (1.14)
Rh-C ₈ H ₉ O ₂ ^b	EtDA	92 (0.74)	68 (1.00)
Rh-C ₁₀ H ₄ Cl ₄ NO ₂ ^c	MeDA	100 (1.00)	
	EtDA	99 (1.06)	58 (1.23)
	<i>n</i> -BuDA	97 (1.20)	
	<i>t</i> -BuDA	99 (1.25)	38 (1.53)
Rh-C ₇ H ₄ F ₃ ^d	MeDA		69 (1.23)
	EtDA	100 (0.75)	86 (1.32)
	<i>n</i> -BuDA		96 (1.53)

Reaction conditions: 22°C; olefin, $3 \cdot 10^{-2}$ mol; catalyst, 10^{-5} mol; diazoester, $3 \cdot 10^{-3}$ mol (perfusion time: 4h). Yields are based on diazoester. Abbreviations (for Table 1 and 2): MeDA, EtDA, *n*-BuDA and *t*-BuDA refer respectively to methyl, ethyl, *n*-butyl and *t*-butyl diazoacetate. Catalyst carboxylate group R': ^a 2,4-dichloro-3,5-dinitrobenzoato-; ^b 2,6-dimethoxybenzoato-; ^c L(+)-2-(tetrachlorophthalimido) propionato-; ^d *meta*-trifluoromethylbenzoato-.

It is worth noting that with 1-b , the thermodynamically less favoured isomer (Z 2-b) predominates. The exact reason for this surprising result is not clear at this time. Purely steric effects can be ruled out in view of the close similarity of the van der Waals radii of methyl groups and chlorine atoms.

It is evident however that halogen atoms at the vinylic position of 1-b play a crucial role.⁵ In the light of those observations, the regio- and stereochemical course of the cyclopropanation of isoprene was then investigated in the presence of two representative catalysts. Again, the cycloaddition is clean, practically quantitative (Table 2) and occurs preferentially (>60%) at the more electron-rich double bond.

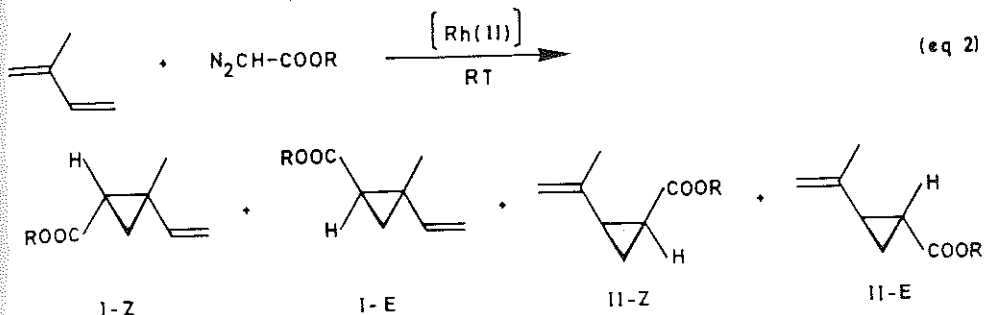


TABLE 2

Rhodium(II) carboxylate-catalysed cyclopropanation of 2-methyl-1,3-butadiene (isoprene).

Rh(II) carboxylate Rh-R'	Alkyl diazooacetate (RDA)	Yield (%) of cyclopropanes	Products distribution (%)				Molar ratios		
			I-Z	I-E	II-Z	II-E	I II	I-Z I-E	II-Z II-E
Rh-CH ₃	MeDA	99	32	30	13	25	1.63	1.07	0.52
	EtDA	93	34	31	11	24	1.86	1.10	0.46
	n-BuDA	88	61	^e	12	27	1.56	^e	0.44
	t-BuDA	85	36	26.5	9.5	28	1.67	1.36	0.34
Rh-C ₁₀ H ₄ Cl ₄ NO ₂ ^e	MeDA	99	26	37	22.5	14.5	1.70	0.70	1.55
	EtDA	98	27	37	20	14	1.94	0.78	1.43
	n-BuDA	99	62	^e	21	17	1.63	^e	1.24
	t-BuDA	95	52	19	14.5	24.5	2.45	2.74	1.00

Reaction conditions and abbreviations as in Table 1.

^e Unresolved g.l.c. peaks.

On the one hand, the *Z* to *E* ratio of the main isomer (I-*Z* to I-*E*) increases steadily with the bulkiness of the diazoester while on the other hand just the opposite trend is observed for isomers II. This observation provides a further indication of the extreme sensitivity of those carbenoid reactions to stereoelectronic parameters, *i.e.* to a very subtle balance between steric, electronic and lipophilic factors in the transition-state, a point clearly apparent in the Rh(II)-catalysed functionalization of paraffins (see accompanying paper) where steric and electronic differences between the *substrates* were kept to a minimum.

In conclusion, this work exemplifies the facile access to pyrethroid precursors via Rh(II)-catalysed decomposition of readily available diazoesters. Proper choice of reaction parameters (diazoester, catalyst) helps determining the stereochemical outcome of the reaction.

EXPERIMENTAL

The general procedures of cyclopropanation as well as the analytical methods were described previously.⁴ The yields and relative ratios of isomers were determined by g.l.c. and all reaction products identified by comparison with authentic samples.

ACKNOWLEDGEMENTS

We thank the Service de la Programmation de la Politique Scientifique, Brussels, for financial support and I.R.S.I.A., Belgium, for a grant to one of us (A.D.). We are also grateful to I.C.I., Agricultural Division for a generous gift of 1,1-dichloro-4-methyl-1,3-pentadiene.

REFERENCES AND NOTES

- (a) M. Elliott, A.W. Farnham, N.F. Janes, P.H. Needham, D.A. Pulman and J.H. Stevenson, *Nature*, **246**, 169 (1973); (b) A. Bader, *Aldrichimica Acta*, **9**, 49 (1976).
- For recent synthetic routes, see for instance: (a) J.P. Genêt, F. Piau and J. Ficini, *Tetrahedron Lett.*, 3183 (1980); J.P. Genêt and F. Piau, *J. Org. Chem.*, **46**, 2414 (1981); (b) H. Lehmkuhl and K. Mehler, *Liebigs Ann. Chem.*, 2244 (1982); (c) R. Lantzsch, *Synthesis*, 955 (1982); (d) R.B. Mitra, Z. Muljiani and A.R.A.S. Deshmukh, *Synth. Commun.*, **12**, 1063 (1982); (e) T.-L. Ho and Z.U. Din, *Ibid.*, **12**, 257 (1982); T.-L. Ho and S.-H. Liu, *Ibid.*, **12**, 995 (1982); T.-L. Ho, *Ibid.*, **13**, 761 (1983); (f) J.H. Babler and R.A. Haack, *Ibid.*, **13**, 905 (1983); (g) J. d'Angelo and G. Revial, *Tetrahedron Lett.*, 2103 (1983); (h) M. Schneider, N. Engel and H. Boensmann, *Angew. Chem. Int. Ed. Engl.*, **23**, 64 (1984).
- (a) J. Farkaš, P. Kouřim and F. Šorm, *Coll. Czech. Chem. Commun.*, **24**, 2230 (1959); (b) D. Holland, D.A. Laidler and D.J. Milner, *J. Mol. Cat.*, **11**, 119 (1981); (c) L. Csiz, 3rd International Symposium on Homogeneous Catalysis, August 30-September 3, 1982, Milano, Abstract Fr 13, p. 183. However, some chiral copper catalysts have been used successfully; (d) T. Aratani, Y. Yoneyoshi and T. Nagase, *Tetrahedron Lett.*, 1707 (1975); (e) *Ibid.*, 2599 (1977); (f) *Ibid.*, 685 (1982).
- (a) A.J. Anciaux, A.J. Hubert, A.F. Noels, N. Petiniot and P. Teyssié, *J. Org. Chem.*, **45**, 695 (1980); (b) A.J. Anciaux, A. Demonceau, A.F. Noels, R. Warin, A.J. Hubert and P. Teyssié, *Tetrahedron*, **39**, 2169 (1983); (c) D. Holland and D.J. Milner, *J. Chem. Research (S)*, 317 (1979); *Ibid. (M)*, 3734 (1979).
- Similar tendency was observed with certain halogeno olefins in the case of 5,5-dichloro-2-methyl-6,6-trifluoro-2-hexene (see ref. 3-b) and by Aratani et al. in the case of 2-methyl-5,5-trichloro-2-pentene (ref. 3-f).