

CHEMISTRY OF METHYL 1-BUTYL-CYCLOPROPENE-3-CARBOXYLATE :
THE ROLE OF TRANSITION METAL IN REACTION CONTROL :
RHODIUM-CATALYSED SYNTHESIS OF A BICYCLOBUTANE, COPPER-
CATALYSED DIMERISATION, SELECTIVE (Tl⁺⁺⁺) OXIDATION.

N. Condé-Petiniot *, A.J. Hubert, A.F. Noels,
R. Warin and Ph. Ieyssié,
Laboratoire de Synthèse Organique et de Catalyse,
Institut de Chimie, Sart Tilman, 4000 Liège 1, Belgium

Received : 03/04/1986 - Accepted : 13/05/1986

SUMMARY

Some typical reactions of a cyclopropenecarboxylate(I) were tentatively controlled by the use of transition metal catalysts. The reaction of (I) with methyl diazoacetate (DAM) afforded a dihydropyrazine(III) which was further dehydrogenated photochemically to the pyrazine(IV) whereas, the bicyclobutane (II) was obtained in the presence of rhodium acetate as catalyst. Copper tri-plate catalysed the ring opening of the cyclopropene ring and a dimer (the octatrienedicarboxylate(V) was thus isolated. Attempts to epoxidize(I) with a peracid (MCPBA) or VO(acac)₂ and MoO(acac)₂-t-butyl hydroperoxide failed. Up to now, only thallium(III) nitrate afforded satisfactory selective oxidation of (I) (formation of the lactone VII).

Cyclopropenes constitute a class of strained and therefore highly reactive molecules. The presence of an endocyclic double bond imparts increased reactivity as compared to cyclopropanes owing to additional strain and the presence of the unsaturation. Therefore, these molecules are prone to typical reactions of olefins such as addition reactions and polymerisation together with rearrangement processes resulting from ring opening reactions.

In a previous note (1), we have reported that the rhodium(II) carboxylates catalysed cycloaddition of carbalkoxycarbenes to "true" acetylenes offers a straight forward synthesis to the disubstituted cyclopropenes(I). As these cyclopropenes were hitherto of very difficult access, their availability prompted us to investigate some aspects of their reactivity.

The most significant observations are summarized in the scheme 1.

a) Bicyclobutane dicarboxylates(II) are of difficult access. They are generally prepared by thermal or photochemical decomposition of pyrazolines (2,3) as well as by the copper catalysed decomposition of diazo-compounds in the presence of an acetylene (4-7). Our present results show that rhodium acetate (Rh₂(OAc)₄=RhAc) affords improved yields (up to 42%) under smooth conditions (25°C instead of 100° with copper) when methyl diazoacetate (DAM) is reacted with 1-hexyne. Two isomers (exo-exo and endo-exo) are formed respectively in 28 and 14% yield. The structure of these isomers was

attributed from their nmr spectra : two different ester methoxy groups are detected in the minor isomer whereas the exo H atom of the cyclobutane ring (α to the endo ester group) appears as a doublet in the spectrum of this isomer. In contrast, the nmr spectrum of the major isomer shows only one type of ester methoxy group. It is noteworthy that the exo-exo isomer is preferably formed in carbalkoxy carbene addition to cyclopropene carboxylate (4-7).

b) Dihydropyridazine dicarboxylate(III) : one of the classical methods of preparation of bicyclobutanes consists in the thermal decomposition of pyrazolines formed by 1,3-dipolar addition of a diazocompound onto a cyclopropene (2,3). However, the reaction of DAM with the cyclopropenecarboxylate(I) led to the formation of the dihydropyridazine(III). This pyridazine is probably formed through the rearrangement of a transient Δ^1 -pyrazoline, the 1,3-dipolar addition product of DAM onto the cyclopropene(I). In fact, such a rearrangement has been reported in the literature (9,10) but is generally observed in the presence of acids or bases (11).

c) Pyridazine dicarboxylate(IV) : irradiation of the dihydropyridazine (III) by UV ($\lambda > 254\text{nm}$ -pyrex filter) affords the pyridazine(IV) and hydrogen.

Therefore, the 1,3-dipolar addition route is not convenient for the preparation of bicyclobutanes in the present case.

d-e) Oxidation of the cyclopropene carboxylate(I) :

Oxidation of (I) with $\text{Tl}(\text{NO}_3)_3$ (12,13) affords the lactone(VII) as the main reaction product together with a small amount of the ketoester(VI). In fact (VI) is an intermediate for the formation of the lactone(VII) : it is well-known that this cyclisation is an acid catalysed reaction (14) and the present oxidation is run under acidic conditions. It is noteworthy that the VII/VI ratio changes with the reaction time (Table I).

Table I
Variation of the lactone(VII) to ketoester(VI) ratio
with reaction time

t (hr)	VII/VI a)
0.25	0.3
4.5	5.2
21.5	13.3

Conditions : Cyclopropene(I) = $\text{Tl}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$
Solvent : methanol. T = 50°C

a) as measured by GLC

Attempts to epoxidize the cyclopropene(I) with peracids (MCPBA) or t-butyl hydroperoxide (VOacac_2 and $\text{MoO}_2\text{acac}_2$ catalysed) failed to give isolable definite products.

f) Copper-catalysed dimerisation of the cyclopropenecarboxylate(I) :

The cyclopropenecarboxylate(I) affords a dimer when stirred at room temperature in the presence of copper triflate in toluene. The formation of the dimer(V) results from a ring opening reaction proceeding probably according to the mechanism proposed by Stechl (15) for the copper(I) chloride catalysed dimerisation of 1,3,3-trimethylcyclopropene to trans-2,3,6,7-tetramethyl-2,4,6-octatriene : the coordination of two cyclopropene to copper would be followed by the ring cleavage with formation of two coordinated vinylcarbenes, the dimerisation of which would lead to the observed product, the stereoselectivity in favour of the trans isomer being controlled by the geometric and steric requirements imposed by the metal.

Other oligomers (dimers and trimers) have also been detected by glc-ms.

Other transition metal based catalysts have been tested : $\text{Ni}(\text{COD})_2$ affords complex mixture of oligomers (dimers and trimers have been detected by glc-ms together with polymers (MW : 1000-10.000)). The Ziegler-Natta catalyst is poorly efficient for initiating the polymerisation of the cyclopropene(I) and insoluble material is obtained. The reaction performed with the metathesis catalyst ($\text{MoCl}_5\text{-AlEt}_3$) affords also the same type of insoluble polymer as in the Ziegler-Natta case whereas the $\text{WCl}_5\text{-Sn}(\text{CH}_3)_4$ system is inactive with this substrate (this last catalyst being active for the metathesis of unsaturated esters (16)).

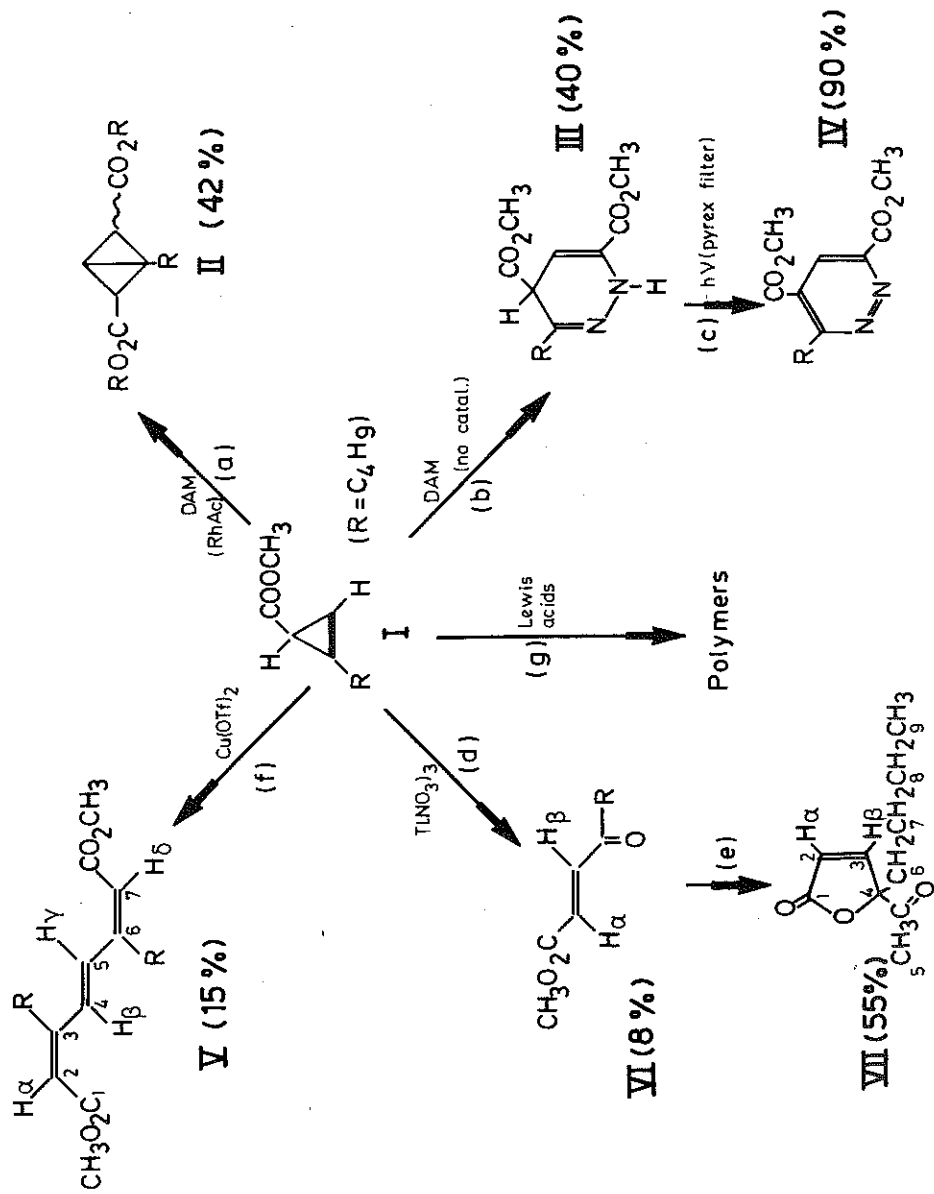
Conclusions

The present study shows therefore that the participation of transition metal catalysts or the use of oxidizing metal ions can be advantageously used to control the reactivity of cyclopropenecarboxylates, a class of reactive and readily available strained molecules.

Some typical reactions such as cyclopropanation to bicyclobutane derivatives, copper-catalysed stereospecific dimerisation and selective oxidation are particularly significant cases of such applications.

Acknowledgements :

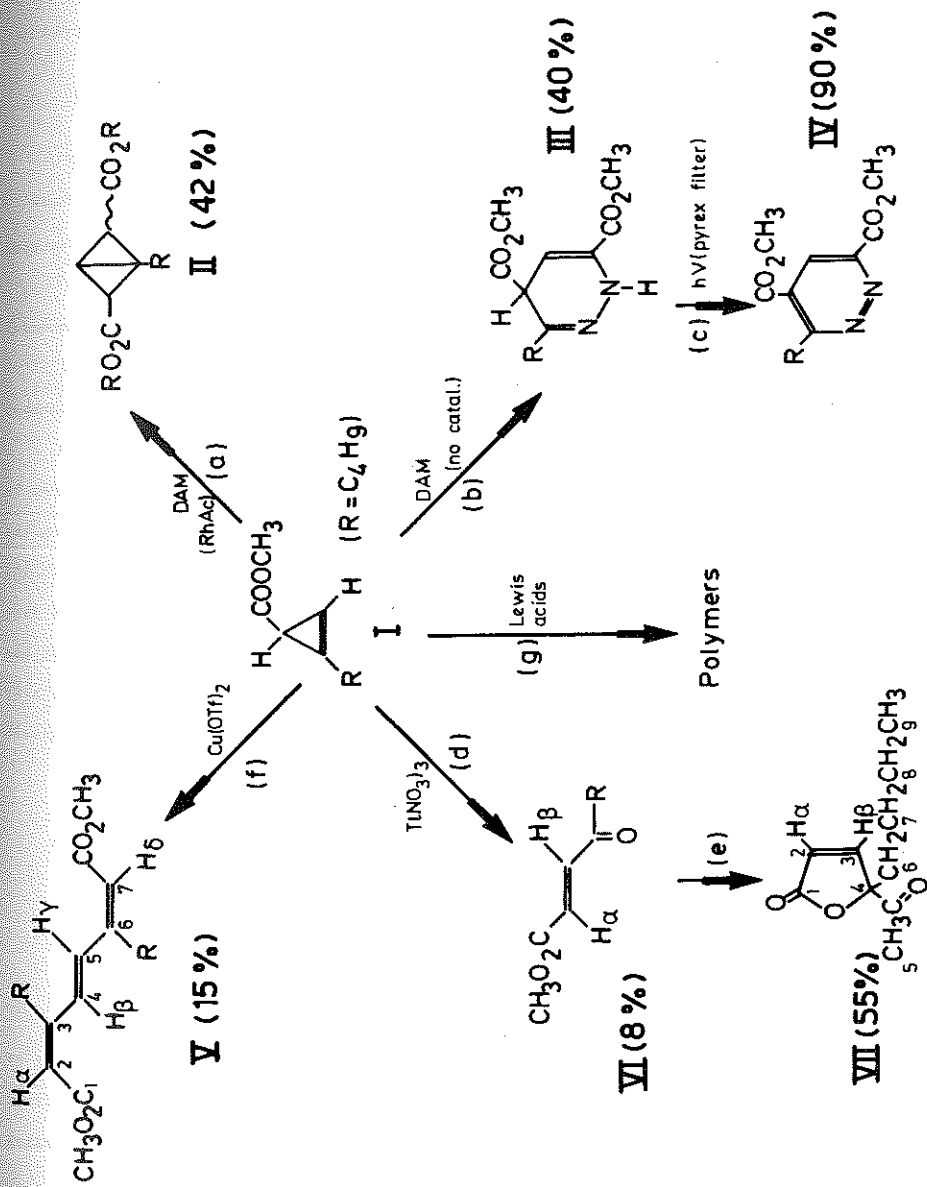
One of us (N. Condé-Petiniot) is indebted to the FNRS (Belgium) for a fellowship; we also acknowledge the support of the "Service de la Programmation de la Politique Scientifique" (Brussels) and the FNRS (Belgium) for a grand (HPLC équipement).



SCHEME I



SCHEME I



SCHEME I

References

- (1) N. Petiniot, A.J. Anciaux, A.F. Noels, A.J. Hubert and Ph. Teyssié; *Tetrahedron Lett.*, **14**, 1239 (1978).
- (2) P.G. Gassman and W.J. Greenlee, *J. Amer. Chem. Soc.*, **95**, 980 (1973).
- (3) M.I. Komendantov, R.R. Bekmkhametov and V.G. Novinskü, *J. Org. Chem. USSR*, **12**, 802 (1976).
- (4) M. Pomerantz and R. Fink, *J. of Labelled Compounds and Radiopharmaceuticals*, **16**, 275 (1979).
- (5) T. Shimadate and Y. Hosomaya, *Bull. Chem. Japan*, **40**, 2971 (1967).
- (6) I.A.D. Yakonow, M.I. Komendantov and V.V. Razin, *J. Gen. Chem. USSR*, **33**, 2360 (1963).
- (7) J.H. Leftin, E. Gilv-Av and A. Pinos, *Chem. Comm.* 396 (1968).
- (8) M. Pomerantz and R. Fink, *J. of Labelled Compounds and Radiopharmaceuticals*, **16**, 275 (1979).
- (9) L.G. Zaitseva, J.B. Averov, O.A. Sublotin and I.G. Bolesov, *Vestn. Mosk. Univ. Khim.*, **15**, 723 (1975); *Chem. Abst.* **82**, 170141 (1975).
- (10) H. Prinzback, *Chimia*, **23**, 37 (1969).
- (11) D.H. Aue, R.B. Lorens and G.S. Helwig, *J. Org. Chem.*, **44**, 1202 (1979).
- (12) A. Mc Killop, J.D. Hunt, E.C. Taylor and F. Kienzele, *Tetrahedron Lett.*, 5275 (1970).
- (13) A. Mc Killop and E.C. Taylor, *Endeavour*, **35**, 88 (1976).
- (14) M.D. Grove and D. Weisleder, *J. Org. Chem.*, **38**, 815 (1973).
- (15) H.H. Stechl, *Chem. Ber.*, **97**, 2681 (1964).
- (16) E. Verkuijlen, R.J. Dirks and C. Boelhouwer. "Proceedings International Symposium on Metathesis", Noordvijkkerhout (Netherlands). *Rec. Rumin, Tetrahedron Lett.*, 1091 (1968).
- (17) P. Courtot and R. Rumin, *Tetrahedron Lett.*, 1091 (1969).
- (18) P. Courtot and R. Rumin, *Bull. Soc. Chim. Fr.*, 3665 (1969).