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EFFECT OF CATALYST ON ZWITTERIONIC INTERMEDIACY IN ADDITIONS OF DIMETHYL DIAZOMALONATE TO VINYL ETHERS

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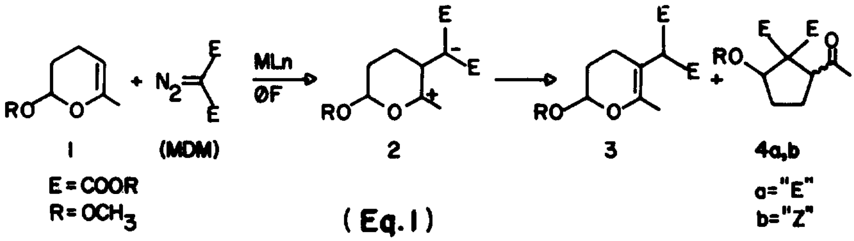
Abstract:

The reaction of dimethyl diazomalonate with 2-alkoxy-6-methyl-3,4-dihydro-2H-pyran in hot fluorobenzene has been studied in the presence of some transition metal catalysts. The characteristic addition-elimination reaction that afforded the 3-malonyl-pyran derivative 3 was found to proceed with the intervention of highly polar species, as indicated by the appearance of skeletal rearrangement products 4a,b that stem from the fragmentation of a carbenium ion at C-2 on the pyran ring. Molecular reorganization was strongly dependent on lingands and metal atom of the catalyst. This was explained as being the consequence of either a polar open-end transition state containing metal catalyst and dimethoxycarbonyl methylene sigma bonded to C-3 of the pyran ring, or as a sigma olefin-metal carbene complex where stabilization of the positive charge is provided by a strong polar interaction with high electron density centers of appropriate ligands.

INTRODUCTION

The chemistry of free and metal associated carbenes continues to be of interest from the mechanistic and synthetic standpoints.[1,2] In spite of the voluminous body of research in the area, there are still open questions regarding the exact chemical behavior of these highly reactive species. Detailed pictures describing the interaction of a given metal catalyst, particularly copper and rhodium, with diazoalkanes en route to metal carbenes, the mechanism of nitrogen extrusion during this step, the precise performance of the metal bonded or free carbene onto alkenic substrates to give cyclopropanation, C-H insertion, addition-elimination or 1,3-dipolar cycloaddition, are not yet complete.

For some time we have studied the degree of concert in the formation of the two C-C bonds between the metal carbene and alkene substrates in copper catalyzed cyclopropanations of some alpha-diazocarbonyl derivatives. Following the early theoretical postulation by Wulfman[3] that, among several possibilities, the metal carbene may interact with the olefin in a non concerted fashion to yield dipolar or diradical intermediates, we derived experimental data suggesting that distinct charge separation could be involved in an intermediate step during cyclopropanation of polarizable olefins.[4] The diradical hypothesis was dismissed in parallel results.[5] In fact, a full carbenium ion was shown to actually intervene during the closely related addition-elimination reaction of dimethyl diazomalonate to enol ethers assisted by copper chelate catalysis.[6] This is illustrated by equation (1). This result has been underscored by the discovery of carbene-alkene adducts in the free carbene series where only one sigma C-C bond is reversibly formed.[7,8] Also, Professor Dewar's contention that cycloadditions in general cannot take place in a concerted fashion[9] brings theoretical support to these observations.



(Eq. 1)

The central role played by the metal catalyst during the entire process from diazocompound to adducts led us to study the influence of various metal complexes on the fate of the reaction above. Now, we have found that skeletal rearrangement of intermediate 2 to give cyclopentane derivatives 4a,b is strongly dependent on metal and ligand components of the catalyst. These results are here disclosed.

RESULTS

Reaction 1 was examined under standard conditions (see experimental) using dimethyl diazomalonate (MDM) that was synthesized in a single batch, and a series of copper(II) and rhodium(II) catalysts, which were added in 2.5% catalyst/diazocompound molar ratio. Results appear collected in Table I.

It was observed that addition-elimination product 3 is formed in comparable yields, irrespective of the catalyst used. Only, and surprisingly, dirhodium tetraacetate (DRTA) gives the poorest yield (55% total adduct yield) in spite of it success in bringing cyclopropanations of diazoesters to nearly quantitative yields, and the short time required for complete MDM decomposition.[10]

TABLE I

INFLUENCE OF CATALYST ON PRODUCT COMPOSITION IN THE REACTION OF DIMETHYL DIAZOMALONATE WITH 1

ENTRY	CATALYST	ACRONYM	REACTION TIME	% YIELD OF: 3	4a	4b
1	$Cu(acac)_2$	ACAC [a)]	8.5 h	74.7	5.4	ND
2	$Cu(F_3acac)_2$	TFAC [b)]	14.0 h	79.2	ND	ND
3	$Cu(F_6acac)_2$	HFAC [c)]	4.0 h	41.1	13.9	38.5
4	$Cu(Phacac)_2$	PhAC [d)]	20 h	79.4	ND	ND
5	$Cu(EtOacac)_2$	EtOAC [e)]	60 h	76.6	ND	ND
6	$CuOTf_2$	CTT [f)]	6.0 h	77.7	ND	ND
7	Rh_2OAc_4	DRTA [g)]	2.5 h	38.9	4.1	8.3

a) Bis-acetoacetonato copper(II); b) Bis-trifluoroacetoacetonato copper(II); c) bis-hexafluoroacetoacetonato copper(II); d) bis- benzoylacetonato copper(II); e) bis-ethoxycarbonylacetonato copper(II); f) copper(II) bis trifluoromethanesulfonate (copper(II) triflate) g) dirhodium tetraacetate; ND= non detected

Catalyst efficiency as measured by time required for complete destruction of the $C{=}N_2$ group, showed a wide spectrum spanning from two to sixty hours. It is apparent from reaction yields that prolongued heating is not detrimental to at least compound 3. Gas chromatograms of reaction mixture samples did not indicate the presence of possibly unstable cyclopentanes 4a,b (owing to steric compression) at early stages during these extended processes. Notably, product composition varied widely depending on the metal organic compound employed. Thus, cyclopentane derivatives were recorded only in additions where HFAC, DRTA, and ACAC were used as catalysts (see Table I for explanation). Although HFAC brought about the highest total adduct yield (93.8%, entry 3 of Table), it showed a less efficient production of addition-elimination adduct 3. Conceivably, the lower yield of 3 could result from the transformation of this compound into cyclopentanes 4 under the auspices of metal catalyst and temperature at a later stage of the reaction. Hence reduced yields of 3 would be expected to be proportional to the increase in cyclopentane formation.

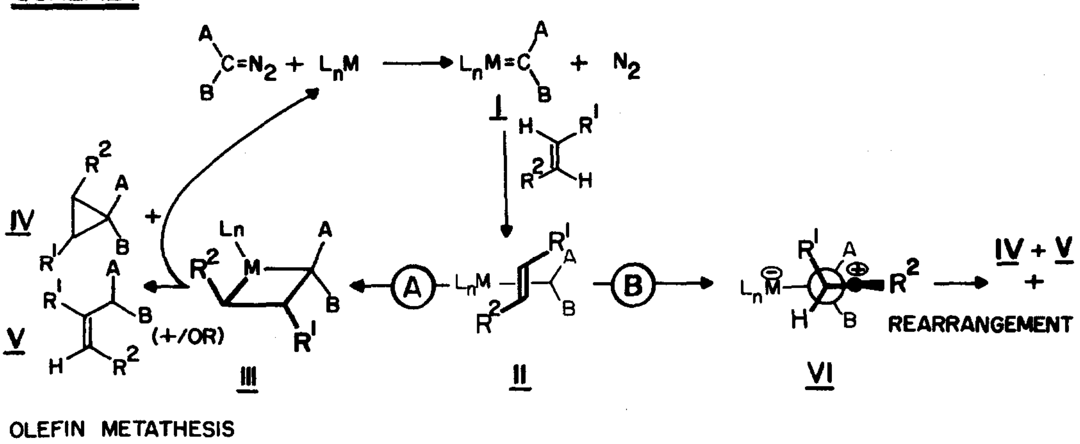
This hypothesis was put to test. A sample containing a mixture of 3 and epimeric 4a,b of known composition was refluxed in degassed fluorobenzene in the presence of a 2.5% molar ratio of HFAC that had been previously exposed to MDM under identical conditions to form the active catalytic species actually present in the reaction. Samples were withdrawn periodically and analyzed (GLC). No apparent change in composition was recorded within experimental error after 6 h heating. In a parallel experiment, a mixture of MDM, olefin 1, and HFAC was examined (GLC) with time. No compositional changes were detected within 2% deviation. These results clearly suggest that addition-elimination leading to 3 and fragmentation-cyclization that furnish 4 are divergent processes stemming from a common carbocationic intermediate.

The skeletal rearrangement was apparently unrelated to the capacity of catalysts to form pi-complexes with the substrate vinyl ether. This was exemplified by the disparate behavior of HFAC and CTT (entries 3 and 6, respectively) in the copper series, and DRTA in rhodium, toward the formation of rearranged products. Both copper chelates are well known for their ability to form complexes with olefins.[12] Contrastingly, ACAC and DRTA, which are devoid of this quality, also promoted strongly polar intermediates albeit to a smaller extent. Notably cyclopentanes were not formed when non-symmetrical chelating ligands were present (entries 2, 4, and 5).

DISCUSSION

Assuming that a rhodium(II) and a copper(I)[13] metal carbenes are formed prior to the intervention of the alkene,[14] presently available evidence allows the proposal of two diverging scenarios that stem from a central, common pi complex II between olefin and metal carbene.[15]

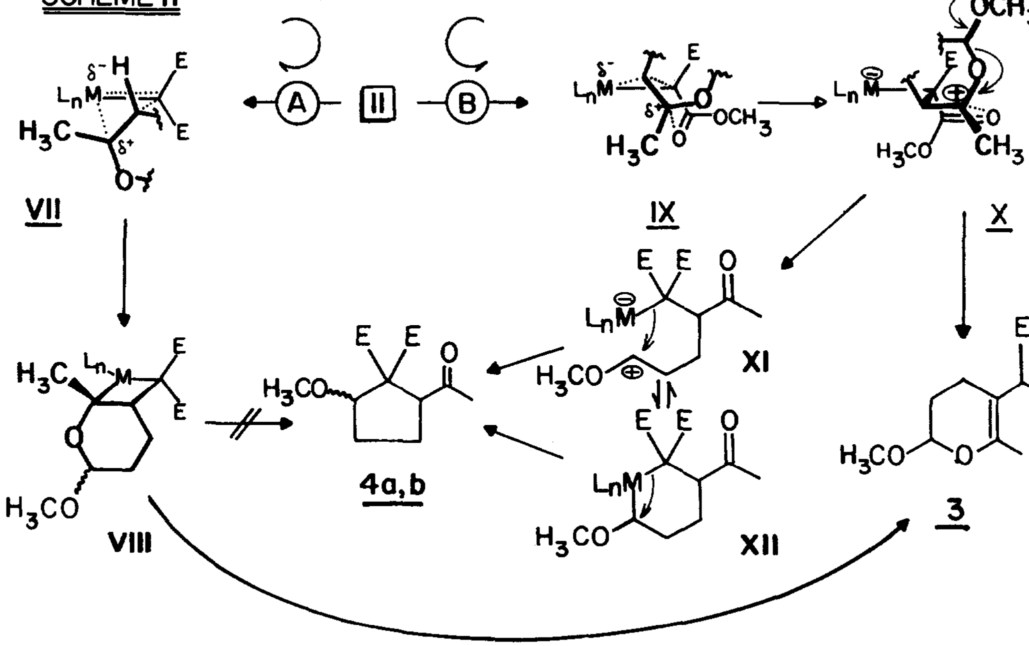
SCHEME I



On the one hand, the orthogonal pi complex turns around to form a planar metallacyclobutane III where the electropositive center of the olefin appears bonded to the metal atom. This structure may give rise to cyclopropanes IV,[16] addition-elimination product V, and olefin metathesis products.[17] Conversely, by turning around in the opposite direction, II may evolve towards an open-end dipolar structure such as VI[1,15a] (Rote B of Scheme I) that equally leads to commonly observed products. Metallocycles such as III have been characterized in a number of cases.[18] It is also known that metal carbene-alkene complexes and metallacyclobutanes coexist in solution.[19] Contrastingly, intermediate VI is until now a theoretical postulation that has been put forward to give satisfactory explanation to steric and electronic factors affecting the stereochemical outcome of cyclopropanation reactions.[15a] In opposition to this, dipolar intermediates have been dismissed on the basis of minor solvent effects on the reaction rate of intramolecular cyclopropanations using tungsten carbenes.[14b]

Now, if it is assumed that a true carbenium ion is a requirement for skeletal rearrangement (2 to 4) to occur, the following should be considered for fitting our results into the accepted picture portrayed in Scheme I. In the first place, if the pi complex II (see Scheme II) in the depicted orientation turns clockwise (route A) the developing positive charge comes in close proximity to the metal atom that is displaying concomitantly a growing negative charge, as in VII. Carbon-metal bonding is likely to occur to give metallocycle VIII. Although the production of 3 by way of proton elimination, and cyclopropanation are both conceivable from this structure, it hardly can lead to fragmentation of the pyran ring to give 4a,b. Indeed, we have attempted unsuccessfully to obtain skeletal rearrangement from metallacyclobutanes of copper(II) and rhodium(II) complexes.[6]

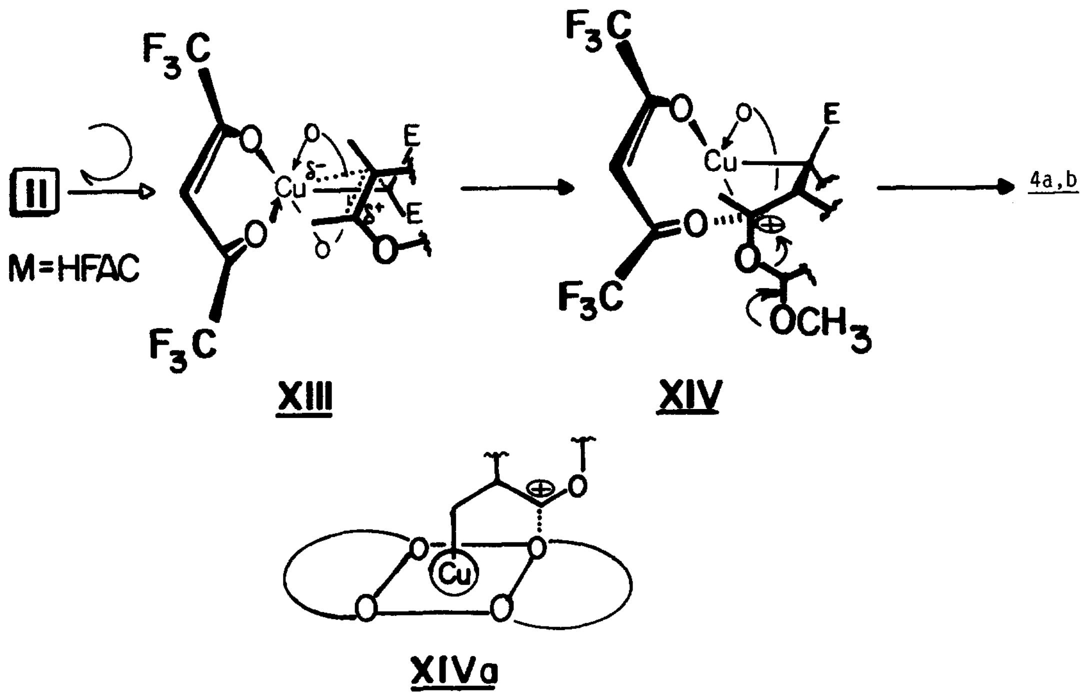
SCHEME II



If, on the contrary, the alkene in II turns counterclockwise (route B), the developing positive carbon will be moving away from the negatively charged metal atom. This movement may be driven by the stabilizing effect of the two carbonyls of the diester portion of the complex as in IX and X. Skeletal unravelling would occur if the carbenium ion in X was sufficiently long lived. Proton elimination may also compete to finish the addition-elimination sequence. Hence, in the absence of other models, only route B of Schemes I and II can account for the production of cyclopentanes 4a,b.

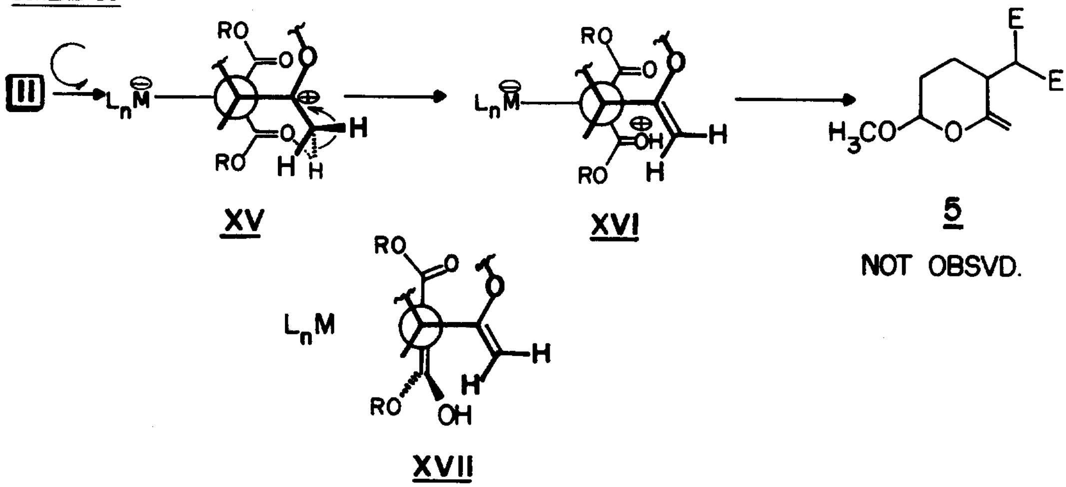
Results of Table I may now be explained in terms of a competitive scenario where the initially formed alkene-metal carbene complex II may follow route A with metallacyclobutane formation, on the one hand, or route B towards polar intermediates on the other, depending on the ligands on the metal atom. Conceivably, the strong electron withdrawing effect of the hexafluoroacetacetonato ligand in HFAC could bring stabilization to LnM(-) thus allowing it to exist as the highly energetic form X. Other less stabilizing ligands would favor the reaction progress towards VII and VIII owing to the concentration of electron density on the metal atom. In addition, the ease of triflate displacement from CTT should facilitate further the construction of VIII, thus promoting addition-elimination only.

SCHEME III



An alternative, third model is still possible. The clockwise turn of complex II may not only lead to LnM(-)/C(+) interaction. Molecular models show that the developing carbenium ion moves toward one of the oxygen atoms of the acetoacetonato ligands at close distance in the planar copper(I) arrangement. This molecular distribution represented by XIV of Scheme III is conceivable for both copper and rhodium (DRTA) complexes. It would provide adequate stabilization of C^+ by the substantial dipole-dipole interaction, that probably would be stronger with certain ligands such as those of entries 3, 7, and 1 in decreasing order. In the absence of a C-MLn bond, the skeletal rearrangement would thus be allowed. Additional evidence that weakens further the hypothesis of route B, at least in this case, is the lack of competitive beta-elimination of a C-6 methyl proton that would lead to apparent allylic C-H insertion product 5, as portrayed in Scheme IV.[15a] This process would be expected to be particularly favorable when a beta-dicarbonyl system such as the malonyl fragment is present. Alkene adduct 5 was carefully looked for in reaction mixtures without success. The results here presented not only show that highly polar, zwitterionic intermediates in metal carbene reactions with appropriate ligands do occur, but also stress the need for further research to assess the validity of route B as a general phenomenon.

SCHEME IV



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EXPERIMENTAL SECTION

Perkin-Elmer 337 and 557 in sodium chloride disks for infrared spectra and Varian T-60 and EM-390 instruments with deuteriochloroform solutions for NMR spectra were used. MDM and 1 were prepared as reported.[6,10] Quantitative determiantions were performed by GLC using a Hewlett-Packard 5910-A instrument fitted with a 12 ft, 3% SE-30 on Chromosorb B, 1/4" packed column and FID, using dimethyl phthalate as internal standard. Independent calibration curves were determined for 3 and 4a,b. The linear plots were represented by equations: $|3|(g)=STD(g)/(-0.066 + 0.333Y)$ and $|4|(g)=STD(g)/(-0.026 + 0.372Y)$ where STD is the internal standard and Y is the ratio of integration values of STD vs. 3 or 4. Experimental deviations of 2.5% were deemed satisfactory.

Reaction of MDM and vinyl ether 1 under catalysis by copper(II) and rhodium(II) complexes:

A solution of MDM (ca. 300 mg) and compound 1 (400 mg, 40% molar excess) was dissolved in degassed fluorobenzene (8 mL) and placed in an addition funnel fitted to a round-bottomed flask equipped with condenser and magnetic stirring under a dry, oxygen-free, nitrogen atmosphere. The flask was charged with the catalyst (2.5 mole %), suspended in fluorobenzene (2 mL), and heated in a constant temperature bath at 75º. Ten drops of the MDM solution was added. The addition was continued only after the first evolution of nitrogen became visible. After two hors of dropwise addition of MDM, the reaction mixture was tested for presence of remaining MDM by IR spectroscopy. Reaction time was recorded when the IR band at 2150 cm^{-1} had completely disappeared. The mixture was then cooled to 0º and passed quickly through a short pad of neutral alumina activity III which was eluted further with chloroform. A measured amount of dimethyl phthalate (ca. 85 mg) was added to the eluate and the mixture was subject to GLC analysis as previously described. Pure compounds 3, 4a, and 4b were purified by preparative TLC and characterized as reported earlier.[6]

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