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METAL-CATALYZED STEREOSPECIFIC RING-OPENING OF 1,2-DIALKYL-3-CARBOMETHOXYCYCLOPROPENES

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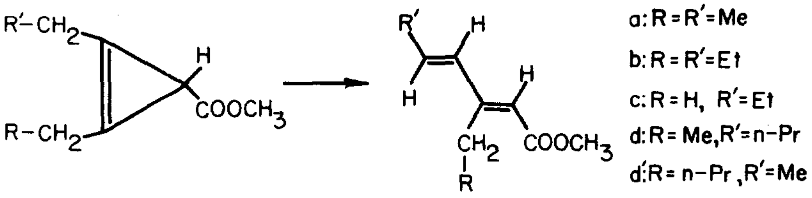
The metal-catalyzed molecular rearrangement of strained ring systems is of considerable current interest (1). We wish now to report the silver-catalyzed rearrangement of 1,2-dialkyl-3-carbomethoxycyclopropenes (I) to methyl 3-alkyl-2,4-dienoates (II).

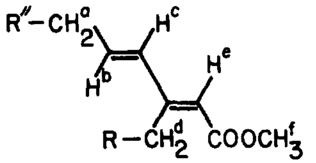


I II

In a typical experiment 1.0 g of 1 c and 0.15 mole-equivalent of $AgClO_4$ were stirred for eight days at 40°. On dissolving in petroleum ether and washing with water, 0.66 g of product containing 84% of IIc was obtained. With 2.0 equivalents of $AgClO_4$, a 62% conversion occurred giving a product containing 94% IIc. Using $AgBF_4$ and temperatures up to 80°, the rate of the reaction can be increased. G.l.c. analysis showed essentially a single peak for products obtained from Ia - Ic, and two peaks (IId and IId') from Id. When the reaction time was unduly prolonged only polymeric material was recovered. No change was observed when Ia was heated under non-catalytic conditions at 220° for 2 hours.

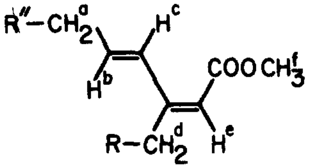
Spectroscopic methods, particularly n.m.r., and synthesis of IIa and the corresponding cis (α, β)-isomer IIIa permitted the elucidation of the structure of compounds II. The trans-geometry of the α, β-double bond was established by the shift to lower field[2] of the proton signals for the methylene or methyl group at the β-carbon, as compared with corresponding signals for IIIa and methyl cis (α, β)-trans (γ, δ)-β-methylsorbate, respectively. The coupling constant of the γ, δ-vinylic protons could not be measured directly, because of their nearly identical chemical shift resulting in a complex splitting pattern (m at ~ 6.1 p.p.m.). Literature (3) is in accord with a trans-geometry of the γ, δ-double bond incorporated into synthetic IIa (and IIIa) via a Reformatzky reaction with trans-propenyl methyl ketone (Table, footnote 1). Since all II compounds have a nearly identical pattern of signals at ~ 6.1 p.p.m., the γ, δ-double bond should be trans throughout.

N.m.r. data (p.p.m., in $CDCl_3$ with TMS as reference)



trans(α, β), trans(γ, δ)-Dienoates

Compound	R''	R	a	b + c	d	e	f
IIa[1]	H	Me	1.87 (d)	~ 6.15 (m)	2.82 (q)	5.72 (s)	3.72 (s)
IIb	Me	Et	2.22 (m)	~ 6.15 (m)	2.80 (t)	5.73 (s)	3.72 (s)
IIc	Me	H	2.20 (m)	~ 6.15 (m)	2.27[2] (s)	5.70 (s)[3]	3.70 (s)
IId	Et	Me	2.20 (m)	~ 6.15 (m)	2.80 (q)	5.71 (s)	3.70 (s)



cis (α, β), trans (γ, δ)-Dienoates

			a	b	c	d	e	f
IIIa[1]	H	Me	1.87 (dd)[4]	6.18 (dq)[5]	7.48 (d)[6]	2.36 (q)	5.58 (s)[3]	3.68 (s)

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1) Also synthesized simultaneously with IIIa by Reformatzky reaction[3] of trans-propenyl methyl ketone with methyl β-bromoacetate followed by dehydration with $POCl_3$;[3] IIa and IIIa were separated by g.l.c.

2) The singlet is superimposed on the multiplet at 2.20; the shift is in accord with that of the β-methyl protons of trans,trans-β-methylsorbate.[4]

3) Broadened due to allylic splitting by H_d.

4) The double doublet is due to splitting by H^b and, allylically, by H^c.

5) $J_{H_bH_c}$ = 16 Hz.

6) Split allylically by H_a.

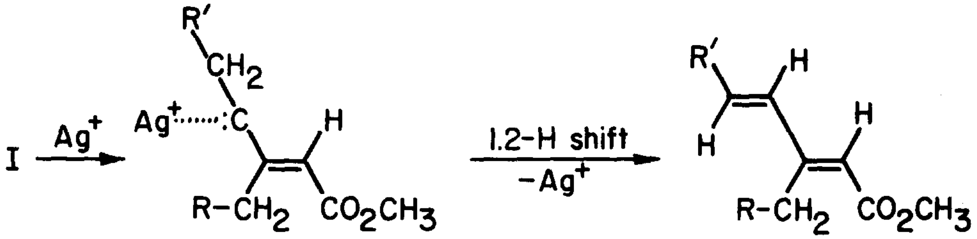
The mass spectra of IIa and IIb showed the expected molecular ion, and fragmentation pattern. IIa has λ_{max} 265 nm (in methanol) [lit. (5), for trans, trans-sorbic acid methyl ester λ_{max} 238 nm (in methanol)].

The conversion of I to II results in ring opening accompanied by the migration of a hydrogen, α to the ring, to the neighbouring carbon (γ-position of II). Compounds I with unequal alkyl groups in the 1- and 2-positions gaive either two (Id → IId + IId'), or one (Ic → IIc) products. The non-formation of β-ethylpentadienoic ester from Ic shows that the reaction involves preferentially migration of a secondary rather than a primary hydrogen.

The presence of the cyclopropenoic double bond seems essential for the reaction, since exo- and endo-7-carbomethoxycarane, as well as 1,2-diethyl-3,4-dicarbomethoxy-cyclobutene remain unchanged under the above experimental conditions. Extremely strong complexation (K ~ 10^7) and polymerization of cyclopropene itself is known to occur with silver ion. (6)

It should be noted that in solvents such as MeOH and $CHCl_3$ additional products seem to form. Also, other metals have been observed to catalyze the reaction at 220° (slowly with Cu; rapidly with PtO_2).

A non-concerted mechanism, such as, e.g., one involving a carbenoid-Ag (I) complex, (1b) could explain the products formed, with the stereospecificity being determined by steric and/or thermodynamic factors.



A similar intermediate has been proposed recently (7) for the oxidative ring opening of 1, 3, 3-trimethylcyclopropene by $Hg(OAc)_2$. An alkenyl carbene intermediate has also been invoked (8) in the dimerization reaction of 1, 3, 3-trimethyl-and 1, 2, 3, 3-tetramethylcyclopropenes by CuCl. Further, it has been reported (9) that in the pyrolysis of the tosylhydrazone of mesityl oxide the intermediate alkenyl carbene gives, in addition to 1, 3, 3-trimethylcyclopropene, 4-methyl-1, 3-pentadiene by a 1, 2-hydrogen shift.

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