8:2). The crude reaction mixture is worked up by column chromatography on silica gel (eluent: benzene/ethyl acetate, variable between 98:2 and 95:5). The isolated compounds are recrystallized or distilled in vacuo. Under these conditions, the separation of 2b from 2d and of 3b from 3c was incomplete; the identification and quantitative evaluation of these compounds were performed by comparison of their [1]H-N.M.R. spectra with those of pure samples prepared from the corresponding morpholines and benzoyl chloride.

Received: May 3, 1976

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Rhodium(II) Carboxylates: Novel Highly Efficient Catalysts for the Cyclopropanation of Alkenes with Alkyl Diazoacetates

André J. Hubert*, Alfred F. Noels, André J. Anciaux, Philippe Teyssié

Université de Liège, Laboratoire de Chimie Macromoléculaire et de Catalyse Organique, Institut de Chimie, Sart Tilman, B-4000 Liège

Copper complexes are widely used as catalysts for the cyclopropanation of alkenes[1]. For example, Salomon and Kochi[2] reported the high efficiency and unusual selectivity of copper(I) triflate in the cyclopropanation of terminal C=C double bonds with alkyl diazoacetates.

In the course of an investigation of the catalytic potential of several group-VIII metal derivatives in such reactions, we observed the high selectivity of palladium(II) acetate as catalyst in the cyclopropanation of monoolefins[3] and in the formation of 1,3-oxazoles[4]. Moreover, the efficiency of rhodium(II) acetate[5] as catalyst in the insertion of carbenes into activated H-bonds constitutes an additional example of the interest of these group-VIII transition-metal complexes in connection with specific problems of synthesis.

We have found that copper(I) triflate and particularly palladium(II) acetate are poor catalysts as far as the cyclopropanation of alkenes substituted at the ethylene group are con-

cerned. We now report on the high efficiency of rhodium(II) carboxylates in the cyclopropanation of this latter type of olefins. The efficiency of the rhodium(II) derivatives depends strongly on their solubilities; therefore, soluble rhodium(II) carboxylates such as the butanoate[6] and the pivalate[6] (the latter being soluble even in pentane) effect high improvements in yields of cyclopropanation products; this applies also to alkenes such as trans-octenes which in the presence of the less soluble rhodium(II) acetate[6] are not cyclopropanated with satisfactory results.
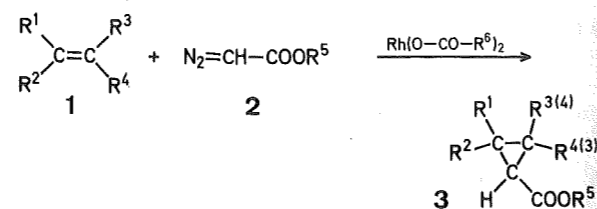
The yields of products 3 also depend strongly on the alkyl diazoacetate (2) used. The best yields are obtained with butyl diazoacetate in the presence of rhodium(II) acetate. This fact may be explained by the increased solubility and stabilization of the intermediately generated carbenoid species.

As expected, solubility of the reaction partners is obviously not the sole factor responsible for the observed efficiency since rhodium(II) trifluoroacetate[7] is well soluble but only poorly efficient (yield: 10–15%), whereas rhodium(II) methoxyacetate[6] gives the same overall results as the acetate. Like in all coordination reactions, the influence of the electronegativity and geometry of the counter-anion are determining. However, steric hindrance at the carboxylate group does not show any major effect on the yield. Such an effect might be expected because of the binuclear nature of the rhodium(II) carboxylates which leaves only one unhindered free coordination site per rhodium atom. A small effect on the stereochemistry of the isomers formed is observed, however. The exo/endo ratio changes from 37:28 to 30:30% (yield of each isomer) when acetate ion is replaced by pivalate ion in the cyclopropanation of cycloocta-1,5-diene.

Moreover, the oxidation state of rhodium plays an important role (possibly by controlling the overall geometry of the complex), as can be concluded from the fact that only very low yields of cyclopropanation products are obtained in the presence of rhodium(III) pivalate[9] or rhodium(I) complexes[8].

The mechanism of the reaction will be discussed elsewhere.

The cyclopropanation products 3 were identified by elemental analyses and by spectral data. In the case of products which differ only in the group R[5], spectral and G.L.C. data alone were used for identification. All alkyl cyclopropanecarboxylates 3 show typical I.R. absorptions of the ester group at $\nu = 1740$ and $1330\,cm^{-1}$. The formation of dialkyl maleates, dialkyl fumarates, or pyrazolines as side products could be excluded by the absence of C=C absorptions in the I.R. spectrum, except for the cyclopropanation products 3o–r obtained from diolefins. The [1]H-N.M.R. spectrum of compounds 3 also showed the absence of any unsaturation (except for 3o–r). The ester group —O—CH₂—R gave a characteristic signal at $\delta = 3.8$–4.1 (t for R=n-C₃H₇, q for R=CH₃) or 3.5 ppm (s for R=H), whereas the remaining protons appeared in the 0.65–2.1 ppm region. The integral ratio of these two groups of protons provides an additional proof of the structure.

Table 1. Alkyl Cyclopropanecarboxylates (3) from Alkenes (1) and Alkyl Diazoacetates (2)[a]

Alkene 1		Product 3					Yield[b] [%] based on 2 and Catalyst used				
		R¹	R²	R³	R⁴	R⁵	R⁶			Cu(II) triflate	Pd(II) acetate
							CH₃	n-C₃H₇	t-C₄H₉		
cis-3-hexene	a[e]	C₂H₅	H	C₂H₅	H	CH₃	56	—	68[d]	—	—
	b[e]					C₂H₅	—	—	—	15	15
	c[e]					n-C₄H₉	98 (90)	—	100[d]	—	—
2,3-dimethyl-but-2-ene	d[f]	CH₃	CH₃	CH₃	CH₃	CH₃	70(28)	—	75(20)[d]	30(36)	<8 (26)
cis-2-octene	e[e]	CH₃	H	n-C₅H₁₁	H	CH₃	65	80[d]	89(12)[d]	40	5 (33)
	f					n-C₄H₉	90[g](82)	—	—	—	—
trans-4-octene	g[e]	n-C₃H₇	H	H	n-C₃H₇	CH₃	7(40)	54(14)[d]	60(40)[d]	8(26)	11.6
	h[e]					C₂H₅	—	—	—	23	
	i					n-C₄H₉	70(30)(58)	—	85(12)[d]	—	
trans-2-octene	j[e]	CH₃	H	H	n-C₅H₁₁	CH₃	24(36)	—	77(20)[d]	14(26)	2.2(18)
	k					n-C₄H₉	70	—	—	—	—
cyclohexene	l[e]					CH₃	84[d](70)	85[d]	—	54	—
	m[e]					C₂H₅	—	—	—	—	21
	n[e]					n-C₄H₉	80[d]		—	64	—
1,5-cyclooctadiene	o[h]					CH₃	(64)(4)[d]	—	60(8)[d]	25(31)	10(30)
2,5-dimethyl-2,4-hexadiene	p[h, i]	CH₃	CH₃	H	C₄H₇	C₂H₅	(85[d])	—	—	77	35
1,3-cyclohexadiene	q[h]	—	—	—	—	C₂H₅	(90[d])	—	—	70	20
1,5-hexadiene	r[h]	H	H	H	C₄H₇	C₂H₅	(80[d])	—	—	60	37

[a] Amounts of components and catalyst used: alkene 1, 10 mmol; alkyl diazoacetate 2, 2.0 mmol; catalyst, 1–2 mg (~0.01 mg-atom of Rh). In the case of the rhodium(II) catalysts, the yields of 3 decrease considerably when more catalyst is used [e.g., from 60% to 15% for 3i when 20 mg instead of 1 mg of rhodium(II) pivalate is used]. This fact may be explained by the fast decomposition observed upon addition of the alkyl diazoacetate to too much catalyst; then, decomposition is complete before the alkyl diazoacetate has sufficiently diluted in the alkene.

[b] Yields are G.L.C. yields; for conditions, see experimental procedure. Underlined yields in (italics) and in brackets are yields of products 3 isolated by distillation. Yield in brackets () are those of the corresponding dialkyl maleates and fumarates formed as side products by (formal) dimerization of the intermediate alkoxycarbonylcarbenes.

[c] These compounds were identified by their I.R.- and [1]H-N.M.R. spectra.

[d] The reactions were carried out in a homogeneous system.

[e] Alkaline hydrolysis of 3c[12] gave 2,3-diethylcyclopropanecarboxylic acid as a mixture of isomers.

C₈H₁₄O₂   calc.   C 67.6   H 9.9
(142.2)   found   66.6   9.9

M.S.: m/e = 142.

[f] The [1]H-N.M.R. spectrum shows the typical signals reported in Ref.[10] for the same compound.

[g] With rhodium(II) methoxyacetate and alkyl diazoacetates 2, R⁵=C₂H₅ and R⁵=n-C₄H₉, the yields of the corresponding alkyl cyclopropanecarboxylates 3 are 20 and 90%, respectively.

[h] Under the conditions employed (excess of olefin, cf. footnote a), monocyclopropanation takes place exclusively.

[i] The [1]H-N.M.R. data were identical with the reported data[14].

Cyclopropanation of Alkenes; General Procedure:

The alkyl diazoacetate (2; 13 mmol) is added slowly (by means of an automatic SAGE syringe) over a period of 10 h to a stirred solution or suspension of the catalyst (0.06 mmol, diazocarboxylate: catalyst = 200) in the olefin (1; 65 mmol) at 20° under a nitrogen atmosphere. The resultant mixture is filtered and the filtrate distilled to give the cyclopropanation product 3 in a purity of at least 95% (by G.L.C.). Further purification (removal of traces of dialkyl maleate and fumarate) is achieved by column chromatography on alumina (elution with benzene followed by ethyl acetate). Analytically pure samples may also be obtained by G.L.C. on FFAP or SE 30 columns.

In the present investigation, the progress of the reaction was followed by G.L.C. on a silicone column (SE 30, 10% on Chromosorb W) and on a FFAP column (10% on Chromosorb W) using a 15°/min program, dibutyl phthalate as an internal standard, and pure authentical samples for identification and quantitative measurements. In a few cases (cis-3-hexene, cis-2-octene, trans-4-octene, cyclohexene), the yields were also determined by distillation.

Table 2. Physical Data of Compounds **3** prepared

3	b.p./torr	b.p./torr from Literature	Brutto formula[a]	Mass spectrum m/e	[1]H-N.M.R. (CDCl3/TMS)[b] δ [ppm]
a					3.50 (s, 3H), 0.7–2.00 (13 H)
b					3.90 (q, 2 H), 0.7–1.70 (16 H)
c	60°/0.01		$C_{12}H_{22}O_2$(198.3)	198	3.92 (t, 2 H), 0.78–1.65 (20 H)
d					3.36 (s, 3H), 1.03–1.1 (35, 13 H)
e					3.50 (s, 3 H, 0.70–1.70 (17 H)
f	90°/0.01		$C_{14}H_{26}O_2$ (226.4)	226	3.95 (t, 2 H), 0.75–1.90 (24 H)
g			$C_{11}H_{20}O_2$ (184.3)	184	3.60 (s, 3 H), 0.80–1.40 (17 H)
h					3.80 (q, 2 H), 0.80–2.00 (20 H)
i	90°/0.01		$C_{14}H_{26}O_2$ (226.4)		3.95 (t, 2 H), 0.80–1.70 (24 H)
j					3.50 (s, 3 H), 0.70–1.70 (17 H)
k			$C_{14}H_{26}O_2$ (226.4)		3.95 (t, 2 H), 0.80–1.70 (24 H)
l					3.40 (s, 3 H), 1.00–1.90 (11 H)
m	50–60°/1	109–110°/18[11]			3.95 (q, 2 H), 1.00–2.10 (14 H)
n			$C_{12}H_{20}O_2$ (196.3)	196	3.86 (t, 2 H), 1.20–1.90 (18 H)
o			$C_{11}H_{16}O_2$ (180.2)	180	5.60 (m, 2 H), 3.67 (s, 3 H), 1.20–2.20 (11 H)
p	56°/6	60°/0.5[13]			4.90 (d, 1 H), 4.10 (q, 2 H), 1.00–2.10 (17 H)
q	72–76°/15	70–75°/15[15]			5.70 (m, 2 H), 4.10 (q, 2 H), 1.00–2.10 (10 H)
r[c]	83°/15		$C_{10}H_{16}O_2$ (168.2)	168	5.80 (m, 1 H), 4.70–5.20 (m, 2 H), 4.10 (q, 2 H), 0.70–2.30 (11 H)

[a] The elemental analyses of compounds **c, f, i, k, o, r** were in satisfactory agreement with the calculated values: C, ±0.33 (0.64 for **c**, 0.51 for **k**); H, ±0.44.
[b] The N.M.R. spectra were recorded with a Varian T-60 spectrometer.
[c] The I.R. spectrum shows the typical ester absorptions at $v = 1728$ and 1330 cm^{-1} whereas the characteristic bands of a CH=CH$_2$ group appear at $v = 990$ and 910 cm^{-1}.

Received: February 18, 1976
(Revised form: May 10, 1976)

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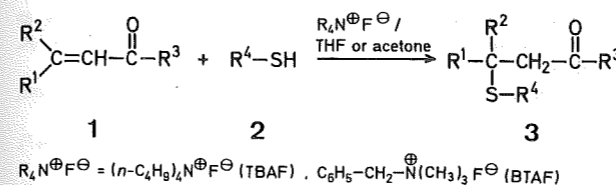[15] J. A. Berson, E. S. Hand, *J. Am. Chem. Soc.* **86**, 1978 (1964).

Quaternary Ammonium Fluoride-Catalyzed Conjugate Addition of Thiols to C=C Double Bonds

Isao KUWAJIMA*, Toshiaki MUROFUSHI, Eiichi NAKAMURA

Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, 152, Japan

Fluoride ion is known to exhibit basic properties especially under aprotic conditions[1]. Except for a few examples[2], however, this fact has until recently not been utilized in organic syntheses, and the strength of the basicity of fluoride ion in aprotic solvents has apparently not yet been investigated thoroughly. During studies on fluoride-catalyzed reactions of organosilicon compounds[3], we found that quaternary ammonium fluoride is an ideal source of fluoride ion[4] in aprotic solvents. This communication describes a fluoride-catalyzed conjugate addition of thiols and the basicity of fluoride ion under aprotic conditions.

In the presence of a catalytic amount of quaternary ammonium fluoride, various thiols (**2**) undergo smooth conjugate addition to α,β-unsaturated carbonyl compounds (**1**) (Table 1). In most cases, the reaction proceeds almost quantitatively, and the crude products **3** are pure except for the presence of very small amounts of fluoride. Various dry aprotic solvents, e.g., ether, tetrahydrofuran, dimethoxyethane, acetone, acetonitrile, and dimethylformamide are employed with equal success. Hydroxylic solvents are inadequate for fluoride-catalyzed reactions, because of the deacti-

vation of fluoride anion by strong hydrogen bonding. In respect of volatility and polarity, acetone, acetonitrile, and tetrahydrofuran are the solvents of choice. In tetrahydrofuran, for example, 0.1—0.03 equiv of the catalyst is needed to obtain a reasonable reaction rate at or below room temperature, yet in more polar solvents the reaction proceeds faster. Among the fluorides examined, tetrabutylammonium fluoride (TBAF) is the best catalyst. Benzyltrimethylammonium fluoride (BTAF)[3], which is prepared from the much cheaper Triton B, has also proved to be a good catalyst.
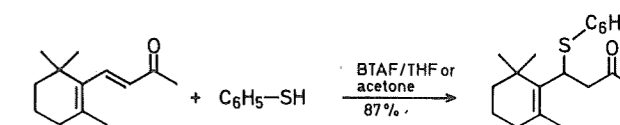
$$R_4N^{\oplus}F^{\ominus} = (n\text{-}C_4H_9)_4N^{\oplus}F^{\ominus} \text{ (TBAF)} \text{ , } C_6H_5\text{-}CH_2\overset{\oplus}{-}N(CH_3)_3 F^{\ominus} \text{ (BTAF)}$$

In this fluoride-catalyzed reaction, the reaction rate is markedly dependent on the structure of both thiol (**2**) and acceptor (**1**) (Table 1). The following example with β-ionone illustrates the regiospecificity caused by such an effect.

Table 1. β-Alkyl(Aryl)thio-carbonyl Compounds (**3**) by Fluoride-Catalyzed Conjugate Addition of Mercaptans (**2**) to α,β-Unsaturated Carbonyl Compounds (**1**)

2	R¹	R²	R³	Catalyst (2–5 mol%)	Reaction conditions (20–25°)	Yield [%]	b.p./torr (bath temperature)	Brutto formula[a] of 3
C6H5—SH	H	H	—COOCH3	TABF	THF/10 min	99	110°/0.04[b]	$C_{10}H_{12}O_2S$ (196.3)
	CH3	H	—COOCH3	BTAF	THF/15 h	83	100°/0.04	$C_{11}H_{14}O_2S$ (210.3)
	H	H	CH3	TBAF	THF/1 h	98	110°/0.07	$C_{10}H_{12}OS$ (180.2)
	CH3	CH3	CH3	TBAF	THF/5 h	94	90°/0.07[d]	$C_{12}H_{16}OS$ (208.2)
	n-C3H7 (trans)	H	H	TBAF	THF/10 min	96	115°/0.15	$C_{12}H_{16}OS$ (208.2)
β-Ionone				BTAF	acetone/7 d	87	140°/0.12	$C_{19}H_{26}OS$ (302.3)
β-Angelica lactone				BTAF	THF/18 h	96	130°/0.06	$C_{11}H_{12}O_2S$ (208.2)
C6H5—CH2—SH	H	H	—COOCH3	TBAF	THF/20 h	87	125/0.15[e]	$C_{11}H_{14}O_2S$ (210.2)
	CH3	H	—COOCH3	BTAF	acetone/20 min	100	115°/0.27	$C_{12}H_{16}O_2S$ (224.2)
	CH3	CH3	CH3	BTAF	THF/2 h	93		
	n-C3H7 (trans)	H	H	TBAF	THF/10 d	79	100°/0.09[f]	$C_{13}H_{18}OS$ (222.2)
				TBAF	THF/30 min	97	110°/0.09	$C_{13}H_{18}OS$ (222.2)
C2H5O—C(O)—CH2—SH	H	H	—COOCH3	TBAF	THF/7 h	85	90°/0.13[g]	$C_8H_{14}O_4S$ (206.2)
	CH3	CH3	CH3	TBAF	THF/2 d	80	90°/0.17	$C_{10}H_{18}O_3S$ (218.2)

[a] All products were characterized by I.R., [1]H-N.M.R., and elemental analysis. The analytical data obtained were in good agreement with the calculated values: C, ±0.3%; H, ±0.3%; S, ±0.3%.
[b] Ref.[6], b.p. 153.5°/12 torr.
[c] Ref.[7], b.p. 105–109°/2 torr.
[d] Ref.[8], b.p. 136–138°/3 torr.
[e] Ref.[6], b.p. 173°/14 torr.
[f] Ref.[9], b.p. 137–138.5°/4 torr.
[g] Ref.[10], b.p. 145–146°/12 torr.

Since the reaction proceeds almost quantitatively, it may be used to estimate the basicity of fluoride ion. A rough estimation of the reaction rate was made for two representative bases (sodium ethoxide and trioctylamine) and TBAF in the reaction of benzyl mercaptan with methyl acrylate. In Table 2 is found a striking difference in the catalytic activity of these reagents. The base-catalyzed addition reaction consists of two sequencial reaction steps, generation and addition of thiolate ion. In these reactions catalyzed by the three bases mentioned, the intermediary thiolate species can be assumed to be of equal reactivity, since the differences between the countercations (Na, R3NH, and R4N) are negligible in regard of the second step of the addition reaction. Thus, the overall rate of the addition reaction should be closely related to the rate of generation of the thiolate ion, which is a measure of the basicity of the catalysts used. Therefore, the results obtained imply that fluoride