Reactions of diazo ketones with activated unsaturated compounds in the presence of gallium trichloride*

R. A. Novikov, Yu. V. Tomilov,* and O. M. Nefedov

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (499) 135 6390. E-mail: tom@ioc.ac.ru

Diazoacetone reacts with methyl acrylate in the presence of anhydrous $GaCl_3$ to give isomeric methyl 2-acetylcyclopropanecarboxylates rather than pyrazolines obtained from diazo esters or by noncatalytic reactions. In a similar reaction, diazoacetophenone yields methyl 2-benzoylcyclopropanecarboxylates, benzoylmethyl acrylate, and benzoylmethyl 2-benzoyl-cyclopropanecarboxylate via partial transesterification. Addition of an equimolar amount of GaCl₃ to diazoacetone in the system CH_2Cl_2 -HCl-H₂O unexpectedly produces 4,5-dimethyl-furan-3(2*H*)-one and 1,1'-oxybis(propan-2-one).

Key words: diazoacetone, diazoacetophenone, cyclopropanes, Lewis acids, transesterification, gallium trichloride.

1,3-Dipolar cycloaddition to unsaturated compounds is a common reaction of aliphatic diazo compounds. Alkenes normally yield 1- or 2-pyrazolines,¹ which can further be transformed into compounds of other types,² including biologically active ones.³ Except for alkenes containing electron-withdrawing substituents or a strained double bond, prolonged keeping or heating is mostly required for these reactions to occur. In some cases, 1.3-dipolar cycloaddition can be promoted by a combination of heating with catalysis by pyridine⁴ or molybdenum hexacarbonyl.⁵ Recently,⁶ we have demonstrated that the rate of cycloaddition of diazo esters to activated alkenes is increased by several orders of magnitude in the presence of some Lewis acids. Specifically, the use of GaCl₃ catalyzes not only 1,3-dipolar cycloaddition but also subsequent insertion of the electrophilic fragment CHCO₂Me of methyl diazoacetate into the N-H bond of the resulting 2-pyrazolines.

Results and Discussion

In the present work, we studied the effects of Lewis acids on diazo ketones as well as on their reactions with activated alkenes. Under normal conditions with no Lewis acids employed, diazoacetone (1a) and diazoacetophenone (1b) slowly and regioselectively react with methyl acrylate (2) according to the 1,3-dipolar cycloaddition

pattern. Isomerization of primary 1-pyrazolines leads to 2-pyrazolines 3a,b, in which the double bond is conjugated with the keto group (Scheme 1).

Scheme 1



Conditions: 25 °C, 3 days.

We tried several Lewis acids (SnCl₄, TiCl₄, BF₃ • Et₂O, EtAlCl₂, In(OTf)₃, Sn(OTf)₂, Yb(OTf)₃, and Sc(OTf)₃) as catalysts for this reaction. However, they all fell short of the expected effect observed earlier⁶ in reactions with diazo esters. For instance, Sc(OTf)₂ and Yb(OTf)₂ increase the rate of the 1,3-dipolar cycloaddition of diazo esters to acrylates by nearly two orders of magnitude⁶ but fail with substrates 1 and 2. The aforementioned tin, titanium, aluminum, boron, and indium compounds promptly break down the starting diazo ketones 1a,b, yet forming no adducts with acrylates. For instance, compounds **1a**,**b** readily react with EtAlCl₂ to give relatively stable organoaluminum intermediates 4a or 4b, which prove to be inert toward an alkene (Scheme 2). When treated with water or methanol, compounds 4 instantaneously eliminate ethane to give α -chloro ketones 5. That is why these Lewis acids are not very convenient for use as catalysts for 1,3-dipolar cycloaddition.

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Reagents and conditions: *i.* $EtAlCl_2$, 1 min, CH_2Cl_2 /hexane; *ii.* MeOY or Y_2O (Y = H, D); *iii.* $GaCl_3$ (H₂O), CH_2Cl_2 , 5 min.

R = Me (a), Ph (b)

Unlike the Lewis acids discussed above, gallium trichloride behaves in a different way. In the absence of water, $GaCl_3$ slowly decomposes diazoacetone into chloroacetone **5a** and unidentified products. When treating compound **1a** with an equimolar amount of $GaCl_3$ in the system CH_2Cl_2 — $HCl-H_2O$, we discovered an unusual transformation of diazoacetone leading to compounds **6** and **7** (Scheme 3).

Scheme 3



Reagents and conditions: GaCl₃ in CH₂Cl₂ and 5% HCl, 5 min.

An intermediate complex of hydroxyacetone with $GaCl_3$ (A), which is formed by partial hydration of compound 1a, seems to be crucial for the formation of furan-3(2*H*)-one 6 and ether 7. Intermediate A attacked by a second diazoacetone molecule on the hydroxy group is transformed into compound 7, while an attack on the carbonyl group of A followed by migration of the methyl group and elimination of water gives furanone 6 (Scheme 4).

Unlike diazoacetone, diazoacetophenone **1b** does not undergo such transformations: its reaction with $GaCl_3$ in both the presence and in the absence of water promptly gives chloroacetophenone **5b** in high yield (see Scheme 2), the process being even promoted by the presence of water.

Nevertheless, gallium trichloride is the only Lewis acid that favors reactions of diazo ketones 1a,b with unsaturated compounds (specifically, with methyl acrylate). As opposed to their noncatalytic transformations, GaCl₃-catalyzed reactions proceed quite rapidly, being completed within 15 min. Unlike diazo esters,⁶ these diazo ketones mostly react by eliminating nitrogen gas. A reaction of diazoacetone with methyl acrylate in the presence of anhydrous GaCl₃ gives cyclopropane derivative 9a as the only intermolecular product. This is a 3.5:1 mixture of E- and Z-isomers (Scheme 5). Unfortunately, much of diazoacetone under these conditions is transformed into chloroacetone 5a. Since the presence of moisture traces appreciably increases its fraction, the yield of cyclopropane 9a is moderate (48-54%) even when the reaction is carried out in a dry inert environment and a threefold excess of methyl acrylate is used (Table 1). The reaction products were isolated by column chromatography on silica gel and identified by ¹H and ¹³C NMR spectroscopy. It should be noted that cyclopropanes are not formed from diazo esters in reactions catalyzed by Lewis acids: the predominant pathway leads to 2-pyrazolines with a multiple increase in the reaction rate.⁶



Scheme 4

Table 1. Reaction products obtained from diazo ketones 1a,b and methyl acrylate (2) in CH_2Cl_2 in the presence of $GaCl_3$

Diazo ketone	Molar ratio of reagents					Yield (%)			
	1	2	GaCl ₃	H ₂ O	-	9	10	11	12
1a	1	3	0.2	_		48	_	_	_
1a	1	3	1	_		54	_	_	_
1b	1	3	0.2	_		36	_	5	_
1b	1	3	1	_		55	3	10	_
1b	1	3	1	2		25	_	52	<5
1b	3	1	1	2		15	_	21	46

Scheme 5



Reagents and conditions: GaCl₃ (H₂O), CH₂Cl₂, 20 °C, 15 min.

As with diazoacetone 1a, a reaction of diazoacetophenone 1b with excess methyl acrylate in the presence of anhydrous GaCl₃ produces chloroacetophenone and cyclopropane 9b as a 2.6 : 1 mixture of *E*- and *Z*-isomers in 36% yield (Scheme 6, see Table 1). The use of an equimolar amount of GaCl₃ increases the yield of cyclopropane 9b to 55%. In addition, small amounts of N-alkylated pyrazoline 10 and isomeric 2-benzoylcyclopropanecarboxylates 11 are detected (see Table 1). Interestingly, while a threefold excess of methyl acrylate (2) is employed, the reaction yields minor products 10 and 11 as a result of the addition of two diazoacetophenone molecules to methyl acrylate.

We assumed that the formation of transalkylated esters 11 could be attributed to moisture traces that persist in the reaction mixture despite great care taken to prevent this. Indeed, the use of two equivalents of water in the reaction of diazoacetophenone 1b with compound 2 in the presence of GaCl₃ substantially changes the ratio of the products (see Table 1). Strange as it may seem, derivative 11 becomes a major product when an excess of methyl acrylate is used and so does compound 12 in the reaction with an excess of the diazo ketone, although the formation of product 12 results from transesterification of methyl acrylate.

Compounds 11 and 12 are both formed by transesterification of methyl carboxylates with diazoacetophenone in the presence of gallium derivatives; in the absence of water, no transesterification occurs. Such processes have not been documented hitherto. Derivative 11 is a ~4 : 1 mixture of *E*- and *Z*-isomers; *i.e.*, its formation is more selective than that of compound 9b. Apparently, the first step involves cyclopropanation of methyl acrylate, which is followed by transesterification of intermediate 9b. The reaction products can easily be separated by column chromatography on silica gel. It should be noted that such processes have not been observed with diazo esters.⁶

To sum up, we were the first to perform direct cyclopropanation of methyl acrylate with diazoacetone and diazoacetophenone in the presence of gallium trichloride. Previous attempts at this cyclopropanation failed because such classic catalysts as copper, palladium, and rhodium derivatives commonly used to decompose diazo compounds are inefficient or unsuitable at all for cyclopropanation of electron-deficient alkenes such as methyl acrylate.

The main role of $GaCl_3$ consists in its coordination to the ester group of methyl acrylate, producing reactive complex **13**. This complex reacts with diazo ketone **1** prior to its decomposition by the Lewis acid (Scheme 7). The first



Reagents and conditions: GaCl₃ (H₂O); CH₂Cl₂, 20 °C, 15 min.

reaction intermediate 14 eliminates a nitrogen molecule so quickly that no cyclization into a pyrazoline ring occurs. (Apparently, similar intermediates formed from diazo esters are much more stable, and their cyclization into pyrazolines is preferred to elimination of N_2 .⁶) The elimination of a nitrogen molecule from compound 14 gives intermediate 15, which undergoes cyclization into cyclopropane 9. Note that the formation of an unsaturated compound by possible deprotonation of intermediate 15 was not observed. In the presence of GaCl₃, compounds 1, 2, and 9, as well as their reaction intermediates, can undergo alternative transformations (*e.g.*, transesterification and NH insertion).

Scheme 7



Experimental

¹H and ¹³C NMR spectra were recorded on a Bruker AMX-400 spectrometer (400.1 and 100.6 MHz, respectively) in CDCl₃ containing 0.05% Me₄Si as an internal standard. The signals were assigned, and the ratio of isomeric reaction products was determined, using homo- and heteronuclear 1D and 2D correlation experiments (DEPT, COSY, NOESY, HSQC, and HMBC). High-resolution mass spectra (ESI-HRMS) were recorded on a micrOTOF instrument. Thin-layer chromatography was carried out on Silufol plates (Merck). For column chromatography, Merck 60 silica gel (0.040–0.063 mm) was used. Anhydrous GaCl₃ was purchased from Aldrich and always handled under dry argon. Reagent-grade solvents (>99.5% purity) were used without further purification. Dichloromethane was dried with granulated KOH and distilled over P_2O_5 under dry argon.

Reactions of diazo ketones 1a,b with EtAlCl₂. A 1 M solution of EtAlCl₂ (1.2 mL, 1.2 mmol) in hexane was added to a stirred solution of diazo ketone 1a or 1b (1 mmol) in CH₂Cl₂ (2.5 mL). The resulting mixture was vigorously stirred at 20 °C for 1 min. Then MeOH or CD₃OD (1 mL) was added. The

reaction mixture was acidified with 10% HCl to pH 1–2, and the product was extracted with CH_2Cl_2 (3×10 mL). The combined organic extracts were dried with MgSO₄ and concentrated *in vacuo* to give chlorinated ketones **5a** or **5b** (or their deuterated analogs). The ¹H and ¹³C NMR spectra of compounds **5a** or **5b** agree with the literature data.^{7–9}

Reaction of diazo ketone 1a with GaCl₃ in the system CH₂Cl₂-HCl-H₂O. A solution of GaCl₃ (314 mg, 1.78 mmol) in CH₂Cl₂ (0.5 mL) was added to a stirred solution of diazoacetone 1a (152 mg, 1.8 mmol) in CH₂Cl₂ (2.5 mL). This was immediately followed by addition of 5% HCl (3 mL). The reaction mixture was vigorously stirred at ~20 °C for 5 min until gas evolution ceased. Organic materials were extracted with CH₂Cl₂ (3×10 mL). The combined organic extracts were dried with anhydrous MgSO₄ and concentrated in vacuo. The residue was separated by column chromatography on silica gel with benzene-AcOEt as an eluent (gradient elution from 5 : 1 to 1 : 10). All products were obtained as colorless oils. They included chloroacetone (5a) (34 mg, 20%), 4,5-dimethylfuran-3(2H)-one (**6**) (35 mg, 34\%), 1,1'-oxydi(propan-2-one) (7) (36 mg, 31%), and 1-hydroxypropan-2one (8) (10 mg, 8%). The ¹H and ¹³C NMR spectra of compounds 5a, 7, and 8 agree with the literature data.^{7,8,10,11}

4,5-Dimethylfuran-3(2*H***)-one (6).** ¹H NMR, δ : 1.68 (s, 3 H, MeC(4)); 2.20 (s, 3 H, MeC(5)); 4.45 (s, 2 H, CH₂). ¹³C NMR, δ : 5.4 (MeC(4)); 15.0 (MeC(5)); 74.0 (CH₂), 111.7 (C(4)); 186.6 (C(5)); 203.3 (C(3)). Found (%): C, 64.08; H, 7.12. C₆H₈O₂. Calculated (%): C, 64.27; H, 7.19.

α-Chloroacetophenone (5b). Anhydrous GaCl₃ (290 mg, 1.64 mmol) was added to a stirred solution of diazoacetophenone **1b** (200 mg, 1.37 mmol) in CH₂Cl₂ (3 mL). The reaction mixture was vigorously stirred at 20 °C for 5 min and acidified with 10% HCl to pH 1–2. The product was extracted with CH₂Cl₂ (3×10 mL). The combined organic extracts were dried with anhydrous MgSO₄ and concentrated *in vacuo*. The yield of α-chloroacetophenone was 192 mg (91%), colorless crystals, m.p. 55–57 °C. The ¹H and ¹³C NMR spectra of compound **5b** agree with the literature data.⁹

Reactions of diazo ketones 1a and 1b with methyl acrylate in the presence of GaCl₃ (general procedure). Anhydrous GaCl₃ (0.2 or 1 mmol, see Table 1) was added in one portion under argon to a stirred solution of diazo ketone 1a or 1b (1 mmol) and methyl acrylate (3 mmol) in dry CH₂Cl₂ (3 mL). The mixture was stirred at 20 °C for 15 min and acidified with 10% HCl to pH 1–2. Organic materials were extracted with CH₂Cl₂ (3×10 mL). The combined organic extracts were dried with anhydrous MgSO₄ and concentrated *in vacuo*. The residue was separated by column chromatography on SiO₂ with benzene—AcOEt (10 : 1) as an eluent. For the yields of the compounds obtained, see Table 1.

Methyl 2-acetylcyclopropanecarboxylate (9a) was obtained from diazoacetone 1a (85 mg, 1 mmol) and methyl acrylate (255 mg, 3 mmol) in the presence of GaCl₃ (34 mg, 0.2 mmol). Yield 68 mg (48%), a ~3.5 : 1 mixture of *E*- and *Z*-isomers (isolated by column chromatography). With an increased amount of GaCl₃ (175 mg, 1 mmol), the yield of compound 9a was 77 mg (54%). The ¹H and ¹³C NMR spectra of this product agree with the literature data.^{12,13}

Methyl 2-benzoylcyclopropanecarboxylate (9b) was obtained from diazoacetophenone 1b (145 mg, 1 mmol) and methyl acrylate (255 mg, 3 mmol) in the presence of GaCl₃ (34 mg, 0.2 mmol). Separation by column chromatography gave isomers E-9b (53 mg, 26%) and Z-9b (21 mg, 10%) and small fractions containing compound **10** (~3%) and a ~4 : 1 mixture of minor cyclopropanes *E*- and *Z*-**11** (~5 or 10%; ¹H NMR data) (see Table 1). With an increased amount of GaCl₃ (175 mg, 1 mmol), the yields of *E*-**9b** and *Z*-**9b** were 82 (40%) and 31 mg (15%), respectively. The ¹H and ¹³C NMR spectra of cyclopropanes *E*-**9b** and *Z*-**9b** agree with the literature data.¹⁴ The procedure for isolation of cyclopropanes *E*- and *Z*-**11** is described below, followed by their characteristics.

Methyl 3-benzoyl-1-(2-oxo-2-phenylethyl)-4,5-dihydro-1*H*pyrazole-5-carboxylate (10). Colorless oil, ~90% purity. ¹H NMR, δ : 3.47 (dd, 1 H, H_a(4), ²*J* = 17.5 Hz, ³*J* = 10.6 Hz); 3.66 (dd, 1 H, H_b(4), ²*J* = 17.5 Hz, ³*J* = 13.4 Hz); 3.78 (s, 3 H, OMe); 4.75 (dd, 1 H, H(5), ³*J* = 13.4 Hz, ³*J* = 10.6 Hz); 5.01 and 5.22 (both d, 1 H each, CH₂, ²*J* = 18.1 Hz); 7.35–7.65 (m, 6 H, *m*-H_{Ph} and *p*-H_{Ph}); 7.96 and 8.07 (both m, 4 H, *o*-H_{Ph}).

Reaction of diazoacetophenone with methyl acrylate in the presence of GaCl₃ and water. *A*. Anhydrous GaCl₃ (125 mg, 0.7 mmol) was added in one portion to a solution of diazoacetophenone (103 mg, 0.7 mmol), methyl acrylate (180 mg, 2.1 mmol), and water (26 mg, 1.4 mmol) in CH₂Cl₂ (3 mL). The reaction mixture was stirred at ~20 °C for 15 min and worked up according to the general procedure. Separation by column chromatography on SiO₂ with benzene—AcOEt (10 : 1) as an eluent afforded compounds *E*-9b (26 mg, 18%), *E*-11 (45 mg, 42%), *Z*-9b (10 mg, 7%), and *Z*-11 (11 mg, 10%) as colorless oils and a small fraction containing compound 12 (<5% yield).

B. A similar reaction of compound **1b** (208 mg, 1.4 mmol) with methyl acrylate (40 mg, 0.48 mmol) in the presence of water (18 mg, 1 mmol) and GaCl₃ (86 mg, 0.48 mmol) gave 2-oxo-2-phenylethyl acrylate (**12**) (42 mg, 46%) as a colorless oil and cyclopropanes *E*- and *Z*-**9b** and *E*- and *Z*-**11** in a total yield of 43 mg (see Table 1). The products were separated by column chromatography on SiO₂ with benzene—AcOEt (10 : 1) as an eluent. The ¹H and ¹³C NMR spectra of compounds **9b** and **12** agree with the literature data.^{14,15}

2-Oxo-2-phenylethyl *E*-2-benzoylcyclopropanecarboxylate (*E*-11). ¹H NMR, δ : 1.70 (ddd, 1 H, H_a(3), ²*J* = 3.7 Hz, ³*J* = 8.5 Hz, ³*J* = 5.7 Hz); 1.74 (ddd, 1 H, H_b(3), ²*J* = 3.7 Hz, ³*J* = 8.5 Hz, ³*J* = 6.0 Hz); 2.55 (ddd, 1 H, H(1), ³*J* = 8.5 Hz, ³*J* = 5.7 Hz, ³*J* = 3.7 Hz); 3.31 (ddd, 1 H, H(2), ³*J* = 8.5 Hz, ³*J* = 6.0 Hz, ³*J* = 3.7 Hz); 5.36 and 5.41 (both d, 1 H each, OCH₂, ²*J* = 16.3 Hz); 7.44-7.65 (m, 6 H, *m*-H_{Ph} and *p*-H_{Ph}); 7.92 and 8.07 (both m, 4 H, *o*-H_{Ph}). ¹³C NMR, δ : 17.9 (C(3)); 24.5 (C(1)); 26.6 (C(2)); 66.5 (OCH₂); 127.9, 128.6, 128.8, and 129.1 (*o*-CH_{Ph} and *m*-CH_{Ph}); 133.5 and 134.1 (2 *p*-CH_{Ph}); 134.4 and 137.2 (2 *ipso*-C_{Ph}); 171.9 (COO); 192.0 and 197.0 (2 CO). C₁₉H₁₆O₄. Calculated: [M + Na], 331.0941. Found: *m*/z 331.0939.

2-Oxo-2-phenylethyl *Z***-2-benzoylcyclopropanecarboxylate** (*Z***-11**). ¹H NMR, δ : 1.48 (ddd, 1 H, H_a(3), ²*J* = 4.8 Hz, ³*J* = 8.6 Hz, ³*J* = 8.5 Hz); 2.01 (ddd, 1 H, H_b(3), ²*J* = 4.8 Hz, ³*J* = 7.1 Hz, ³*J* = 6.7 Hz); 2.51 (ddd, 1 H, H(1), ³*J* = 8.7 Hz, ³*J* = 8.5 Hz, ³*J* = 6.7 Hz); 2.89 (ddd, 1 H, H(2), ³*J* = 8.7 Hz, ³*J* = 8.6 Hz, ³*J* = 7.1 Hz); 5.18 and 5.28 (both d, 1 H each, OCH₂, ²*J* = 16.4 Hz); 7.36–7.60 (m, 6 H, *m*-H_{ph} and *p*-H_{ph}); 7.83 and 8.04 (both m, 4 H, $o-H_{Ph}$). ¹³C NMR, δ : 12.6 (C(3)); 22.8 (C(1)); 26.5 (C(2)); 66.4 (OCH₂); 127.9, 128.5, 128.7, and 129.0 ($o-CH_{Ph}$ and $m-CH_{Ph}$); 133.3 and 133.9 (2 $p-CH_{Ph}$); 134.2 and 136.7 (2 *ipso-C*_{Ph}); 169.7 (COO); 192.1 and 194.8 (2 CO). C₁₉H₁₆O₄. Calculated: [M + Na], 331.0941. Found: m/z 331.0937.

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