2-Azido-1,3-dimethylimidazolinium Salts: Efficient Diazo-Transfer Reagents for 1,3-Dicarbonyl Compounds

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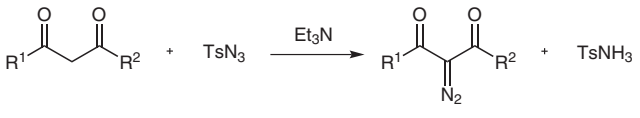
Abstract: We have developed the diazo-transfer of 2-azido-1,3-dimethylimidazolinium salts to 1,3-dicarbonyl compounds. 2-Azido-1,3-dimethylimidazolinium chloride (ADMC) was prepared by N-nitrosation of *N*-aminoguanidine or by the reaction of 2-chloro-1,3-dimethylimidazolinium chloride (DMC) and sodium azide. The corresponding phosphate, ADMP, was isolated as a crystal, and was found to be a stable and safe reagent. Both ADMC and ADMP reacted with 1,3-dicarbonyl compounds under mild conditions to give 2-diazo-1,3-dicarbonyl compounds in high yields, which are easily isolated because the by-products are highly soluble in water.

Key words: azides, diazo compounds, diazonium salts, diazo-transfer, heterocycles

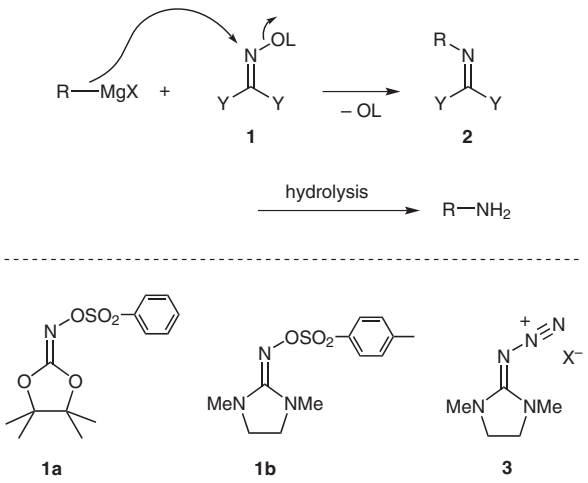
α-Diazocarbonyl compounds are often used in organic synthesis because of their unique characteristic reactivity, and have been used, for example, in cyclopropanation, C–H insertion, and Wolff rearrangement via carbene or carbenoid formation.[1]

Diazo group transfer to an active methylene group is a useful synthetic approach to the synthesis of α-diazocarbonyl compounds. The technique using sulfonyl azides has been named the Regitz diazo-transfer method and is especially applied to the synthesis of 2-diazo-1,3-dicarbonyl compounds.[2,3] *p*-Toluenesulfonyl azide (tosyl azide) is commonly used as the transfer reagent.[3] However, the reaction using tosyl azide frequently raises the problem of isolation of the desired diazo compound from excess tosyl azide and sulfonamide, which is a by-product of the diazo-transfer using tosyl azide (Scheme 1).[4] Furthermore, tosyl azide was reported to be hazardous due to its impact-sensitivity and low initiation temperature.[5] To overcome the drawbacks associated with the use of tosyl azide, several modified diazo-transfer reagents have been reported.[6]

We previously examined the electrophilic amination of Grignard reagents with oxime derivatives,[7] such as 1,3-dioxolan-2-one *O*-phenylsulfonyloxime (**1a**)[8] and 1,3-dimethyl-2-imidazolidinone *O*-tosyloxime (**1b**).[9] Various primary amines were prepared by the reaction of oxime **1** and Grignard reagents with subsequent hydrolysis of the resulting imines **2** (Scheme 2). Oxime **1a** was a better electrophilic reagent than oxime **1b** for the synthesis of primary amines because the hydrolysis of the imines **2** derived from **1b** required harsh basic conditions (CsOH, ethylene glycol, 150 °C). However, during the first step, i.e., the reaction with the Grignard reagent, was oxime **1b** more effective than oxime **1a** for the formation of the C–N bond. At –78 °C, oxime **1b** could react with alkyl Grignard reagents; however, it was not employed for the electrophilic amination of relatively low nucleophilic reagents such as enolate.



Scheme 1 Diazo-transfer of tosyl azide to 1,3-dicarbonyl compounds



Scheme 2 Electrophilic amination with oximes

We designed guanidino diazonium salt **3** (azido-dimethylimidazolinium salt) as an efficient electrophilic aminating reagent. This compound has nitrogen (N_2) as a leaving group instead of the sulfonyl group of oxime **1b**. However, although **3** did not demonstrate any aminating ability, it did facilitate diazo-transfer to 1,3-dicarbonyl compounds. In a previous report, we reported the results briefly.[10,11] In this article, we describe the results in detail.

For the preparation of 2-azido-1,3-dimethylimidazolinium chloride (ADMC; **3a**), we devised the following two methods (Scheme 3): N-nitrosation of *N*-aminoguanidine **4** (method A) and substitution of 2-chloro-1,3-dimethylimidazolinium chloride (DMC; **5a**)[12] with an azide ion (method B).

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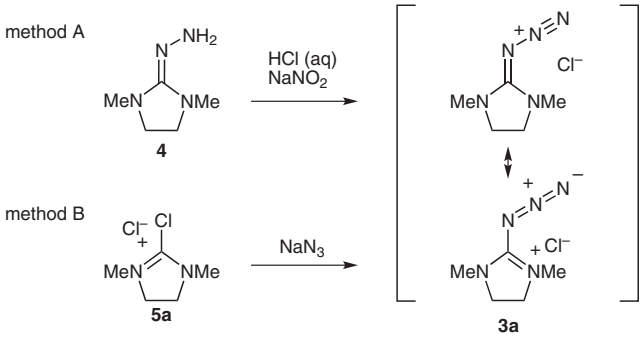
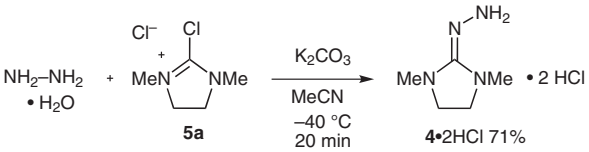


Scheme 3 Synthetic plan for the synthesis of ADMC **3a**

First, we examined the preparation of ADMC (**3a**) by method A and the reaction of **3a** with 1-phenylbutane-1,3-dione (**6**). The starting hydrazone **4** was prepared as its hydrochloride salt by the reaction of commercially available chloroimidazolinium **5a** and hydrazine hydrate in acetonitrile in the presence of potassium carbonate (Equation 1).[13]

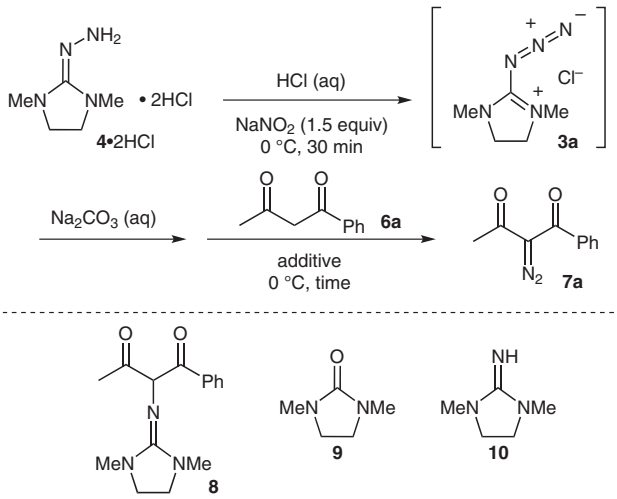


Equation 1

To an aqueous hydrochloric acid solution of guanidine **4**, sodium nitrite was added at 0 °C (Table 1). After stirring the mixture for 30 min, saturated aqueous Na_2CO_3 solution was added until the pH exceeded 10. To the solution, 1-phenylbutane-1,3-dione (**6a**) was then added under several conditions. When the diketone **6a** was added with the same amount of triethylamine, the mixture became a suspension. After stirring for one hour, diazo compound **7a** was obtained in 67% yield (entry 1), however, the formation of the expected aminated compound **8** was not observed. Using a two-fold excess of triethylamine, the yield of **7a** increased to 85% (entry 2). When tetrahydrofuran was added as a co-solvent, the reaction mixture became a single phase, and the diazotized product **7a** was obtained in 92% yield, even in the absence of triethylamine (entry 3). By adding a two-fold excess of triethylamine and tetrahydrofuran, ketone **6a** was consumed within 10 minutes, and the diazo compound **7a** was obtained quantitatively (entry 4).

We then examined the preparation of ADMC (**3a**) by method B (Scheme 4). The salt **3a** was prepared by the reaction of chloroimidazolinium salt **5a** and sodium azide in acetonitrile at 0 °C.[14] To the mixture, triethylamine and 1-phenylbutane-1,3-dione (**6a**) in tetrahydrofuran were added at 0 °C. The ketone **6a** was consumed within 10 minutes, and diazo compound **7a** was obtained in 98% yield. The formation of salt **3a** was confirmed by mass spectral analysis; the FAB (positive) mass spectrum of the mixture

Table 1 Reaction of **6a** with **3a** Prepared by Method A

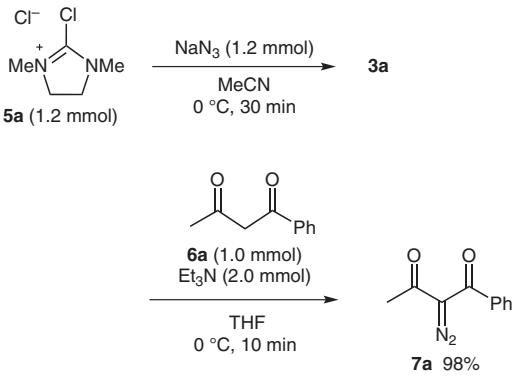


Entry	Additive	Time (min)	Yield of **7a** (%)[a]
1	Et_3N (1.0 equiv)	60	67
2	Et_3N (2.0 equiv)	60	85
3	THF	60	92
4	Et_3N (2.0 equiv), THF	10	quant.

[a] Isolated yield.

of the chloroimidazolinium salt **5a** and sodium azide showed a peak (m/z = 140) that corresponded to the calculated mass of $[\mathbf{3a} - Cl]^+$.

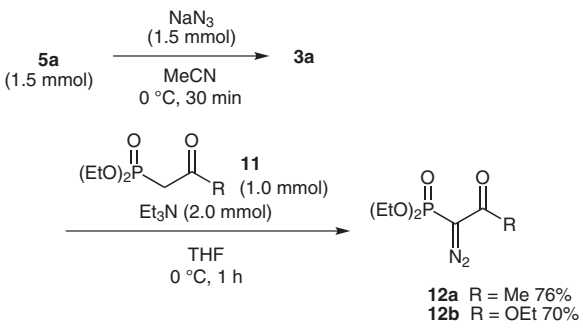
In diazotization reactions using ADMC (**3a**) formed by both methods A and B, we observed the formation of 2-imidazolidinone **9**. The mechanism of formation of **9** was unclear, although **9** could be formed by hydrolysis of an excess of azidoimidazolinium salt **3a** and/or guanidine 1,3-dimethyl-2-iminoimidazolidine (**10**). Because 2-imidazolidinone **9** was highly soluble in water, washing an organic extract of the reaction mixture with water separated the by-product **9** from diazo compound **7a**. This contrasts to the diazo-transfer reaction using tosyl azide, in which it is often difficult to separate the by-product from the diazo compound.



Scheme 4 Reaction of 1-phenylbutane-1,3-dione (**6a**) with azidoimidazolinium salt **3a** prepared by method B.

To examine the scope and limitations of this method, we then investigated the diazotization of various 1,3-dicarbonyl compounds (Table 2). Diketones and a ketoester reacted smoothly with azidoimidazolinium **3a** to give the corresponding diazo compounds in high yields (entries 1–4). Although the reaction required longer reaction times when ketoamide or diester was employed, the diazo products were obtained in high yields (entries 5 and 6). Cyclic 1,3-dicarbonyl compounds were also diazotized by using this approach (entries 7–9).

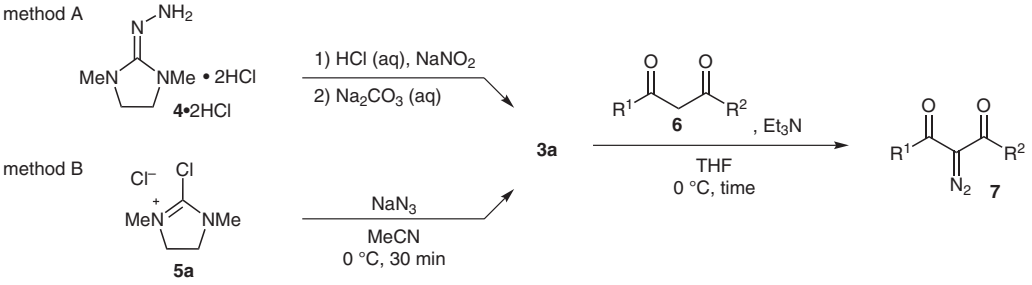
We also examined the diazotization of β-carbonyl phosphate (Scheme 5). The Ohira–Bestmann reagent[15] **12a** was successfully prepared by the reaction of ADMC (**3a**) with diethyl (2-oxopropyl)phosphonate (**11a**) in 76% yield. Triethyl phosphonoacetate (**11b**) gave the corresponding diazo compound **12b** in 70% yield.

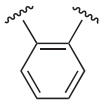


Scheme 5 Diazotization of β-carbonyl phosphate

As mentioned above, we developed two ways to prepare ADMC (**3a**), which was generated before the diazo-transfer reaction from **4**·2HCl or **5a** by methods A or B, respectively. These starting materials, **4**·2HCl and **5a**, are both sensitive to moisture and are relatively difficult to handle. Therefore, we anticipated that if the 2-azido-1,3-dimethylimidazolinium salt **3a** could be isolated as a stable compound, the reaction using the salt could be performed more conveniently. However, isolation of 2-azido-1,3-dimethylimidazolinium chloride (ADMC; **3a**) proved to be problematic because of its hygroscopic character. We then examined the synthesis of various 2-azido-1,3-dimethylimidazolinium salts **3** with different counter anions in an attempt to achieve their isolation (Table 3). The synthesis of hexafluorophosphate (2-azido-1,3-dimethylimidazolinium hexafluorophosphate; ADMP; **3b**) was first attempted.[16] Following a modification of the procedure developed by Kiso and co-workers,[17] the anion exchange

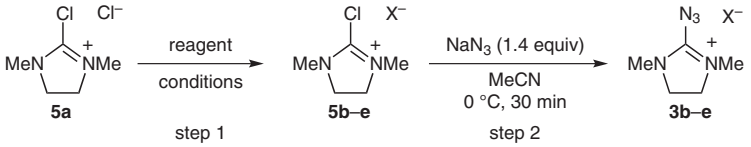
Table 2 Diazo-Transfer Reaction to 1,3-Dicarbonyl Compounds with ADMC (**3a**)



					Method A[a]		Method B[b]	
Entry	R^1	R^2	**6**	**7**	Time (min)	Yield (%)[c]	Time (min)	Yield (%)[c]
1	Me	Ph	**6a**	**7a**	10	quant.	10	98
2	Me	Me	**6b**	**7b**	10	91	10	93
3	Ph	Ph	**6c**	**7c**	3 h	96	2 h	99
4	Me	OEt	**6d**	**7d**	10	84	2 h	82
5	Me	NMe_2	**6e**	**7e**	3 h	91	4 h	79
6	OEt	OEt	**6f**	**7f**	22 h	86[d]	4 h	99
7	$–CH_2C(Me)_2CH_2–$		**6g**	**7g**	3 h	91	10	94
8	$–OC(Me)_2O–$		**6h**	**7h**	10	92	10	95
9			**6i**	**7i**	10	85	–	–

[a] Molar ratio: **4**·2HCl/$NaNO_2$/1,3-dicarbonyl compounds/Et_3N = 1:1.5:1:2.
[b] Molar ratio: **5a**/NaN_3/1,3-dicarbonyl compounds/Et_3N = 1.2:1.2:1:2.
[c] Isolated yield.
[d] Et_3N (3 equiv) was used.

Table 3 Preparation of Various 2-Azido-1,3-dimethylimidazolinium Salts



Entry	X^-	Reagent (equiv)	Conditions	Step 1	Yield (%)[a]	Step 2	Yield (%)[a]
1	PF_6^-	KPF_6 (1.0)	MeCN, r.t., 10 min	**5b**	94	**3b**	quant.
2	BF_4^-	KBF_4 (0.92)	MeCN, r.t., 10 min	**5c**	51	**3c**	95[b]
3	$CF_3SO_3^-$	$LiOSO_2CF_3$ (0.67)	MeCN, r.t., 10 min	**5d**	66		
4	$SbCl_6^-$	$SbCl_5$ (1.0)	CH_2Cl_2, 0 °C, 2 h	**5e**	90	**3e**	80

[a] Isolated yield.
[b] Two-step yield without isolation of **5c**.

of **5a** was accomplished by treatment of KPF_6 in acetonitrile, to afford chloroimidazolinium hexafluorophosphate **5b** (entry 1). The reaction of **5b** and sodium azide in acetonitrile and subsequent re-precipitation by addition of diethyl ether, afforded 2-azido-1,3-dimethylimidazolinium hexafluorophosphate (ADMP; **3b**) quantitatively. Salt **3b** could be stored in a freezer (–10 °C) and showed the same reactivity after at least two months. In a similar manner, we examined the synthesis of various azide salts with different counter anions. By treatment of KBF_4 with **5a**, the corresponding tetrafluoroborate **5c** was isolated in 51% yield (entry 2). Although we could not isolate imidazolinium tetrafluoroborate **3c** in a manner similar to that of **3b** from **5c** due to the formation of a small amount of gummy material, **3c** was isolated from **5a** in 95% yield by a one-pot procedure without the isolation of **5c**. Triflate **5d** (X = OTf) was synthesized and isolated, whereas **5d** was found to easily decompose and was not stored (entry 3). Hexachloroantimonate **5e** was obtained in a good yield by the reaction of $SbCl_5$ and **5a**, and was transformed into azide **3e** in 80% yield (entry 4).

For ADMP **3b**, we performed impact[18] and friction-sensitivity tests,[19] which showed that salt **3b** tested negative to explosion hazard in a range of the tests. Figure 1 depicts the results of the differential scanning calorimetry (DSC) experiment with **3b**; exothermic decomposition was observed from approximately 200 °C. These results suggested that **3b** could be used at temperatures below its decomposition temperature, preferably below 100 °C with a sufficiently large margin.

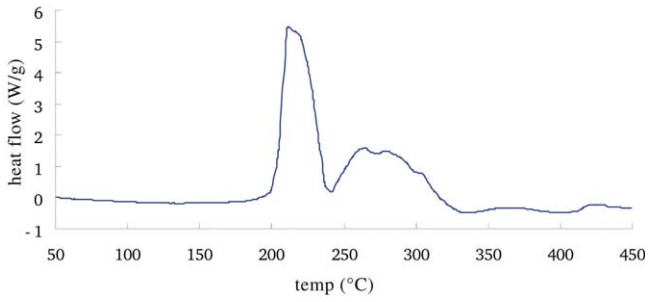
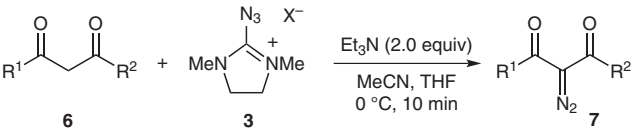
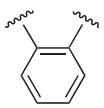


Figure 1 DSC measurement of ADMP (**3b**); heating rate: 10 K/min; sample size: 3.36 mg; argon atmosphere, open Al pan

We then examined the diazo-transfer reaction to 1,3-dicarbonyl compounds using the isolated salts **3b**, **3c**, and **3e** (Table 4). Entries 1–3 show the results obtained with 1-phenylbutane-1,3-dione (**6**). The reaction with hexafluorophosphate **3b** (ADMP) and tetrafluoroborate **3c** proceeded smoothly, while **3e** was not suitable for diazotization. Phosphate **3b** was easier to use than tetrafluoroborate because of its low hygroscopic character, and could even be used in air for a short time. Therefore,

Table 4 Diazo-Transfer Reaction to 1,3-Dicarbonyl Compounds with Isolated 2-Azido-1,3-dimethylimidazolinium Salt **3**

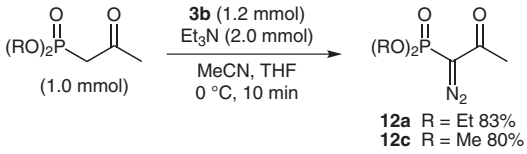


Entry	R^1	R^2	X^-	**3**	Yield (%)[a]
1	Me	Ph	PF_6^-	**3b**	91
2	Me	Ph	BF_4^-	**3c**	95
3[b]	Me	Ph	$SbCl_6^-$	**3e**	20
4	Me	Me	PF_6^-	**3b**	83
5	Ph	Ph	PF_6^-	**3b**	90
6	Me	OEt	PF_6^-	**3b**	99
7	Me	NMe_2	PF_6^-	**3b**	91
8	OEt	OEt	PF_6^-	**3b**	quant.
9	$–CH_2C(Me)_2CH_2–$		PF_6^-	**3b**	86
10	$–OC(Me)_2O–$		PF_6^-	**3b**	78
11			PF_6^-	**3b**	78

[a] Isolated yield.
[b] The reaction was carried out at r.t. for 2.5 h.

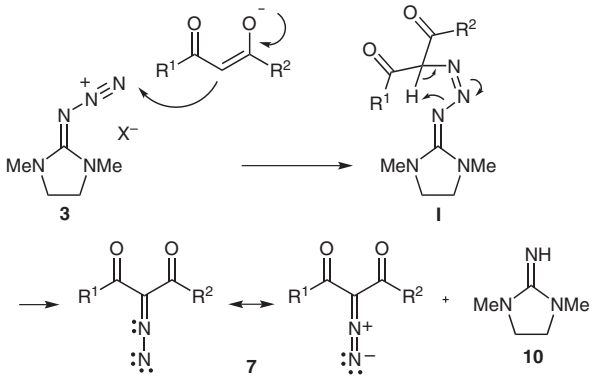
for further studies on the reaction with isolated 2-azido-1,3-dimethylimidazolinium salt **3**, we chose to use ADMP (**3b**) as the diazo-transfer reagent (entries 4–11). All the reactions of 1,3-dicarbonyl compounds with ADMP (**3b**) that were examined proceeded within 10 minutes and gave the corresponding diazo-compounds in good yields.

The Ohira–Bestmann reagent **12a** and **12c** were also prepared by the reaction of ADMP (**3b**) in high yields (Equation 2).



Equation 2

Scheme 6 shows a plausible reaction mechanism. In this pathway, the enolate formed from proton abstraction from the 1,3-dicarbonyl compound by the base, attacks the end of the nitrogen in **3** to form intermediate **I**. Intramolecular proton abstraction in **I** then occurs to afford the corresponding diazo compound **7** and guanidine **10**.



Scheme 6 Plausible reaction mechanism

In conclusion, an efficient diazotization method for 1,3-dicarbonyl compounds using 2-azido-1,3-dimethylimidazolinium salts **3** has been developed. Azido-1,3-dimethylimidazolinium chloride (ADMC; **3a**) was prepared by N-nitrosation of *N*-aminoguanidine **4** or by the reaction of commercially available DMC (**5a**) and sodium azide before use. The corresponding phosphate ADMP **3b** was isolated as a safe crystal. From this diazotization, 2-diazo-1,3-dicarbonyl compounds were obtained in high yields and were easily isolated because the by-products are highly soluble in water.

Caution! Although we have never had any trouble with azidoimidazolinium salt **3**, it is potentially explosive.

All reactions were carried out under an argon atmosphere unless otherwise noted. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with a Bruker Avance 400 spectrometer; ^{13}C NMR (126 MHz) spectra were recorded with a JEOL JNM-A 500 spectrometer in $CDCl_3$, DMSO-d_6 or CD_3CN solutions [$CHCl_3$ (^{1}H; δ = 7.24 ppm) or $CDCl_3$ (^{13}C; δ = 77.0 ppm), DMSO-d_6 (^{1}H; δ = 2.50 ppm) or DMSO-d_6 (for ^{13}C, δ = 40.0 ppm), CH_3CN (for ^{1}H, δ = 1.90 ppm) or CD_3CN (for ^{13}C, δ = 1.30 ppm) were used as internal standard]. IR spectra were recorded with a JEOL JIR-WINSPEC50.

High-resolution mass spectra were obtained with a JEOL JMS-SX102A mass spectrometer. The melting points are reported uncorrected. Elemental analyses were recorded with a Yanaco MT-5, and were carried out at the Center for Instrumental Analysis, Faculty of Engineering, Kyusyu Institute of Technology. Column chromatography was performed on silica gel (Fuji Silysia Silica gel PSQ-100B or BW300). Differential scanning calorimetry (DSC) was recorded with a RIGAKU Thermo Plus2 DSC 8270.

1,3-Dimethylimidazolidinonehydrazone Dihydrochloride (4·2HCl)

To a solution of hydrazine hydrate (2.0 mL, 41 mmol) and K_2CO_3 (5.78 g, 41.8 mmol) in MeCN (20 mL) at 0 °C, a solution of 2-chloro-1,3-dimethylimidazolinium chloride (**3**; 4.59 g, 27.2 mmol) in MeCN (20 mL) was added, and the mixture was stirred for 30 min. The mixture was filtered through a Celite pad (washed with MeCN) and the filtrate was concentrated in vacuo. The residue was dissolved with a small amount of MeCN and the solution was poured into diethyl ether to form a precipitate, which was collected by suction filtration to afford hygroscopic 1,3-dimethylimidazolidinonehydrazone dihydrochloride (**4**·2HCl) in 71% yield. The amount of HCl contained within the hydrochloride salt of **4** was estimated by elemental analysis of the salt.

IR (Nujol): 1456 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.50 (s, 4 H), 3.08 (s, 6 H).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.21 (s, 2 H), 3.60 (s, 4 H), 3.31 (s, 6 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 158.5, 49.5, 35.1.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 49.4, 35.3.

Anal. Calcd for $C_5H_{14}Cl_2N_4$: C, 29.86; H, 7.02; N, 27.86. Found: C, 30.71; H, 7.51; N, 27.46.

Typical Procedure (Method A)

To a solution of 1,3-dimethylimidazolidinonehydrazone dihydrochloride (**4**·2HCl; 1.15 mmol) in H_2O (2.5 mL) was added concd HCl (5.5 mmol). Sodium nitrite (1.5 mmol) in H_2O (1 mL) was added slowly at 0 °C, and the mixture was stirred for 20 min. To the mixture was added aq Na_2CO_3 until pH >10, then a solution of 1,3-dicarbonyl compound (1.0 mmol) and Et_3N (2.0 mmol) in THF (3.5 mL) was added to the mixture, which was stirred for 10 min. Organic materials were extracted with CH_2Cl_2 (3 × 15 mL) and the combined extracts were washed with brine (15 mL) and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo to afford the crude compound, which was purified by flash column chromatography (silica gel; hexane–EtOAc) to give the pure 2-diazo-1,3-dicarbonyl compound.

Typical Procedure (Method B)

To a solution of 2-chloro-1,3-dimethylimidazolinium chloride (**3**; 1.2 mmol) in MeCN (2 mL), sodium azide (1.2 mmol) was added at 0 °C, and the mixture was stirred for 30 min. 1,3-Dicarbonyl compound (1.0 mmol) and Et_3N (2.0 mmol) in THF (4 mL) was added to the mixture, which was stirred until the 1,3-dicarbonyl compound was consumed (reaction monitored by TLC). The reaction was quenched with H_2O (5 mL), and the organic materials were extracted with CH_2Cl_2 (3 × 15 mL). The combined extracts were washed with H_2O (3 × 20 mL) and brine (15 mL), and then dried over anhydrous Na_2SO_4. The solvent was removed in vacuo to afford the almost-pure diazo compound. The crude material was further puri-

fied by flash column chromatography (silica gel; hexane–EtOAc) to give the pure 2-diazo-1,3-dicarbonyl compound.

2-Diazo-1-phenylbutane-1,3-dione (7a)[6l]
IR (Nujol): 2114, 1651 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.65 (m, 2 H), 7.58 (tt, *J* = 7.4, 1.6 Hz, 1 H), 7.50 (m, 2 H), 2.58 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.7, 185.0, 137.3, 132.6, 128.9, 127.3, 83.7, 29.2.

Anal. Calcd for $C_{10}H_8N_2O_2$: C, 63.82; H, 4.28; N, 14.89. Found: C, 63.81; H, 4.38; N, 14.81.

2-Diazopentane-1,3-dione (7b)
IR (neat): 2368, 2268, 2125, 1666, 1225, 1136, 1049, 1024 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.2, 84.5, 28.4.

HRMS (EI): *m*/*z* calcd for $C_5H_6N_2O_2$:126.0429; found: 126.0435.

2-Diazo-1,3-diphenylpropane-1,3-dione (7c)[6k]
IR (Nujol): 2117, 1641, 1595, 1317, 1261, 1174 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.2 Hz, 4 H), 7.44 (t, *J* = 7.4 Hz, 2 H), 7.31 (t, *J* = 7.8 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.4, 137.0, 132.6, 128.4, 128.3, 84.4.

Anal. Calcd for $C_{10}H_8N_2O_2$: C, 71.99; H, 4.03; N, 11.19. Found C, 71.90; H, 4.17; N, 11.21.

Ethyl 2-Diazo-3-oxobutyrate (7d)[6l]
IR (neat): 2985, 2937, 2393, 2134, 1726, 1660, 1651, 1373, 1319, 1176, 1074, 1022 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.31 (q, *J* = 7.1 Hz, 2 H), 2.48 (s, 3 H), 1.34 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.1, 161.3, 76.3, 61.3, 28.1, 14.2.

HRMS (EI): *m*/*z* calcd for $C_6H_8N_2O_3$:156.0535; found: 156.0523.

2-Diazo-3-oxobutyric Acid *N*,*N*-Dimethyl Amide (7e)
IR (neat): 3473, 2112, 1633, 1497, 1398, 1298, 1057 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.02 (s, 6 H), 2.36 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.3, 161.1, 73.1, 37.3, 27.0.

HRMS (FAB): *m*/*z* $[M + H]^+$ calcd for $C_6H_9N_3O_2$:156.0773; found: 156.0800.

Diethyl 2-Diazomalonate (7f)[6l]
IR (neat): 2985, 2141, 1765, 1373, 1323, 1095 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.31 (q, *J* = 7.1 Hz, 4 H), 1.32 (t, *J* = 7.1 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.9, 65.3, 61.5, 14.2.

HRMS (EI): *m*/*z* calcd for $C_7H_{10}N_2O_4$:186.0641; found: 186.0659.

2-Diazo-5,5-dimethylcyclohexane-1,3-dione (7g)[6g]
IR (Nujol): 2359, 2341, 2189, 2137, 1660, 1633, 1306, 1277, 1265 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 4 H), 1.13 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.8, 83.7, 50.5, 31.1, 28.3.

Anal. Calcd for $C_{10}H_8N_2O_2$: C, 57.82; H, 6.07; N, 16.86. Found C, 57.84; H, 6.06; N, 16.74.

5-Diazo-2,2-dimethyl-1,3-dioxane-4,6-dione (7h)[6l]
IR (Nujol): 2177, 1714, 1194, 1167 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.79 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2, 107.0, 64.9, 26.7.

Anal. Calcd for $C_{10}H_8N_2O_2$: C, 42.36; H, 3.55; N, 16.47. Found: C, 42.34; H, 3.59; N, 16.43.

2-Diazoindane-1,3-dione (7i)[6g]
IR (Nujol): 2127, 1682, 1545 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.86 (m, 2 H), 7.75–7.77 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.1, 137.0, 134.7, 122.6, 70.1.

Diethyl 1-Diazo-2-oxopropylphosphonate (12a)[6k]
IR (neat): 2987, 2119, 1659, 1269 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.28–4.16 (m, 4 H), 2.29 (s, 3 H), 1.40 (dt, *J* = 7.1, 0.6 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.8 (d, *J* = 13.2 Hz), 63.2 (d, *J* = 5.6 Hz), 27.0, 15.9 (d, *J* = 6.7 Hz).

HRMS (EI): *m*/*z* calcd for $C_7H_{13}N_2O_4P$: 220.0613; found: 220.0595.

Ethyl Diazo(diethoxyphosphoryl)acetate (12b)[20a,b]
IR (neat): 2133, 1705, 1479, 1446, 1392, 1369, 1306 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.17–4.30 (m, 6 H), 1.37 (t, *J* = 7.1 Hz, 6 H), 1.31 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.4 (d, *J* = 48.8 Hz), 63.6 (d, *J* = 23.2 Hz), 61.6, 16.1 (d, *J* = 27.6 Hz), 14.3.

HRMS (EI): *m*/*z* calcd for $C_8H_{15}N_2O_5P$: 250.0719; found: 250.0707.

Dimethyl 1-Diazo-2-oxopropylphosphonate (12c)[20c]
IR (neat): 2854, 2123, 1660, 1363, 1273, 1028 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.86 (d, *J* = 11.9 Hz, 6 H), 2.28 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.6 (d, *J* = 12.9 Hz), 53.4 (d, *J* = 5.6 Hz), 26.9.

HRMS (EI): *m*/*z* calcd for $C_5H_9N_2O_4P$: 192.0300; found: 192.0270.

2-Chloro-1,3-dimethylimidazolinium Hexafluorophosphate (5b)[17b]
To a solution of 2-chloro-1,3-dimethylimidazolinium chloride (**5a**; 1.24 g, 7.3 mmol) in MeCN (2 mL) was added potassium hexafluorophosphate (1.32 g, 7.2 mmol) in MeCN (5 mL), and the mixture was stirred for 10 min at r.t. The mixture was filtered through a Celite pad and the filtrate was concentrated in vacuo. The residue was dissolved with a small amount of MeCN (ca. 2 mL) and the solution was poured into Et_2O to form a precipitate, which was collected by suction filtration to afford chloroimidazolinium hexafluorophosphate **5b**.

Yield: 1.91 g (94%); mp 230–231 °C.

IR (Nujol): 2362, 2320, 1641, 1551, 1338, 1308 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 3.89 (s, 4 H), 3.08 (s, 6 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 35.2, 50.9.

Anal. Calcd for $C_5H_{10}ClF_6N_2P$: C, 21.56; H, 3.62; N, 10.06. Found: C, 21.29; H, 3.48; N, 9.73.

2-Azido-1,3-dimethylimidazolinium Hexafluorophosphate (ADMP; 3b)

To a solution of chloroimidazolinium hexafluorophosphate (**5b**; 2.35 g, 7.8 mmol) in MeCN (8 mL), sodium azide (717 mg, 11 mmol) was added at 0 °C, and the mixture was stirred for 30 min. The mixture was filtered through a Celite pad and the filtrate was concentrated in vacuo. The residue was dissolved in a small amount of MeCN (ca. 2 mL) and the solution was poured into Et_2O to form a precipitate, which was collected by suction filtration to afford the title compound.

Yield: 2.27 g (quant.); mp 203–205 °C (dec.).

IR (Nujol): 2360, 2173, 1647, 1578 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 3.74 (s, 4 H), 3.01 (s, 6 H).

^{13}C NMR (126 MHz, CD_3CN): δ = 156.6, 55.0, 33.8.

Anal Calcd for $C_5H_{10}F_6N_5P$: C, 21.06; H, 3.54; N, 24.56. Found: C, 21.07; H, 3.42; N, 24.27.

2-Chloro-1,3-dimethylimidazolinium Tetrafluoroborate (5c)

To a solution of 2-chloro-1,3-dimethylimidazolinium chloride (**5a**; 274.3 mg, 1.6 mmol) in MeCN (1.5 mL), was added potassium tetrafluoroborate (184.7 mg, 1.47 mmol) in MeCN (1.5 mL), and the mixture was stirred for 10 min at r.t. The mixture was filtered through a Celite pad and the filtrate was concentrated in vacuo. The residue was dissolved with a small amount of MeCN (ca. 1 mL) and the solution was poured into Et_2O to form a precipitate, which was collected by suction filtration to afford chloroimidazolinium tetrafluoroborate **5c**.

Yield: 169.2 mg (51%); mp 140–150 °C.

IR (ATR): 1641, 1543, 1300, 1053 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.13 (s, 4 H), 3.24 (s, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 156.3, 50.3, 35.0.

Anal. Calcd for $C_5H_{10}BClF_4N_2$: C, 27.25; H, 4.57; N, 12.71. Found: C, 27.04; H, 4.42; N, 12.59.

2-Azido-1,3-dimethylimidazolinium Tetrafluoroborate (3c)

To a solution of 2-chloro-1,3-dimethylimidazolinium chloride (**5a**; 811 mg, 4.8 mmol) in MeCN (1.0 mL), was added potassium tetrafluoroborate (594 mg, 4.7 mmol) in MeCN (4.0 mL), and the mixture was stirred for 10 min at r.t. Sodium azide (426 mg, 6.5 mmol) was added to the solution, which was stirred 30 min at 0 °C. The mixture was filtered through a Celite pad and the filtrate was concentrated in vacuo. The residue was dissolved with a small amount of MeCN (ca. 1 mL) and the solution was poured into Et_2O to form a precipitate, which was collected by suction filtration to afford **3c**.

Yield: 1.01 g (95%); mp 74–78 °C (dec.).

IR (ATR): 2173, 1639, 1571, 1423, 1381, 1306, 1051 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.94 (s, 4 H), 3.16 (s, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.6, 49.1, 33.3.

Anal Calcd for $C_5H_{10}BF_4N_5$: C, 26.46; H, 4.44; N, 30.86. Found: C, 25.65; H, 4.68; N, 28.77.

2-Chloro-1,3-dimethylimidazolinium Triflate (5d)

To a solution of 2-chloro-1,3-dimethylimidazolinium chloride (**5a**; 950 mg, 5.6 mmol) in MeCN (3 mL), was added lithium triflate (597 mg, 3.8 mmol) in MeCN (3 mL), and the mixture was stirred for 10 min at r.t. The mixture was filtered through a Celite pad and the filtrate was concentrated in vacuo. The residue was dissolved in a small amount of MeCN (ca. 2 mL) and the solution was poured into Et_2O to form a precipitate, which was collected by suction filtration to afford chloroimidazolinium triflate **5d**.

Yield: 707 mg (66%).

IR (ATR): 1635, 1543, 1456, 1261, 1171, 1032 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.19 (s, 4 H), 3.26 (s, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 156.4, 50.3, 35.1.

HRMS (EI): *m/z* calcd for $C_5H_{10}{}^{35}ClN_2$:133.0533; found: 133.0526. Calcd for $C_5H_{10}{}^{37}ClN_2$:135.0503; found: 135.0513.

2-Chloro-1,3-dimethylimidazolinium Hexachloroantimonate (5e)

To a solution of 2-chloro-1,3-dimethylimidazolinium chloride (**5a**; 1.28 g, 7.62 mmol) in CH_2Cl_2 (8 mL) was added antimony(V) chloride (1.0 mL, 7.9 mmol) in CH_2Cl_2 (8 mL), and the mixture was stirred for 2 h at 0 °C. The mixture was filtered through a Celite pad and the filtrate was concentrated in vacuo. The residue was dissolved in a small amount of MeCN (ca. 2 mL) and the solution was poured into Et_2O to form a precipitate, which was collected by suction filtration to afford chloroimidazolinium hexachloroantimonate **5e**.

Yield: 3.20 g (90%); mp 266–268 °C.

IR (ATR): 1625, 1537, 1299 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 3.16 (s, 4 H), 2.59 (s, 6 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.0, 44.9, 31.6.

2-Azido-1,3-dimethylimidazolinium Hexachloroantimonate (3e)

To a solution of chloroimidazolinium hexachloroantimonate (**5e**; 0.466 g, 0.995 mmol) in MeCN (3 mL), sodium azide (0.102 g, 1.57 mmol) was added at 0 °C, and the mixture was stirred for 1 h. The mixture was filtered through a Celite pad and the filtrate was concentrated in vacuo. The residue was dissolved in a small amount of MeCN and the solution was poured into Et_2O to form a precipitate, which was collected by suction filtration to afford 2-azido-1,3-dimethylimidazolinium hexachloroantimonate **3e**.

Yield: 0.36 g (76%); mp 227–230 °C (dec.).

IR (ATR): 2163, 1600, 1421, 1251 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 3.79 (s, 4 H), 3.05 (s, 6 H)

^{13}C NMR (100 MHz, DMSO-d_6): δ = 155.5, 49.2, 33.4

Anal Calcd for $C_5H_{10}Cl_6N_5Sb$: C, 12.65; H, 2.12; N, 14.75. Found: C, 12.62; H, 2.06; N, 15.03.

Reaction of 1,3-Dicarbonylcompounds and Isolated 3b; Typical Procedure

2-Azido-1,3-dimethylimidazolinium hexafluorophosphate (ADMP, **3b**; 0.6 mmol) in MeCN (0.5 mL) was cooled to 0 °C. A solution of 1,3-dicarbonyl compound (0.5 mmol) and Et_3N (1.0 mmol) in THF (2.0 mL) was added and the reaction was stirred for 10 min. The reaction was quenched with H_2O (5 mL), and the organic materials were extracted with CH_2Cl_2 (3 × 10 mL). The combined extracts were washed with brine (15 mL), and then dried over anhydrous Na_2SO_4. The solvent was removed in vacuo to afford the almost pure diazo compound. The crude material was purified by flash column chromatography (silica gel; hexane–EtOAc) to give the pure 2-diazo-1,3-dicarbonyl compound.

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