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Cyclopropanation of electron-deficient alkenes with activated dibromomethylene compounds mediated by lithium iodide or tetrabutylammonium salts

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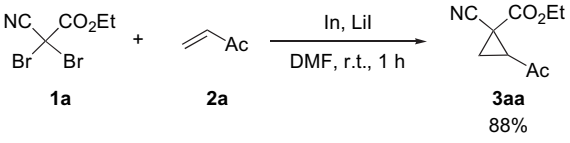
ABSTRACT

Reactions of electron-deficient alkenes with dibromomethylene compounds activated by cyano and ester groups were promoted by LiI or tetrabutylammonium bromide to afford the corresponding cyclopropanes in high yields.

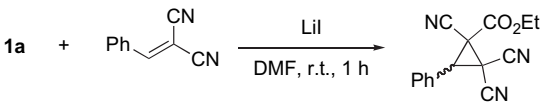
1. Introduction

The cyclopropane subunit is an important building block of a large number of biologically active compounds.[1] Its properties as well as practical syntheses have been a great concern to organic chemists.[2] Previously we reported that indium-mediated reactions of electron-deficient alkenes with active methylene dibromides in the presence of LiI afforded the corresponding cyclopropanes in high yields (Eq. 1).[3]



1a **2a** **3aa** 88% (1)

Without LiI the yield was rather diminished. During the course of re-screening the reaction conditions, we found that, the presence of indium metal is not necessary for promoting the reaction, and only a stoichiometric amount of LiI is enough to facilitate the cyclopropanation (Eq. 2).[4]



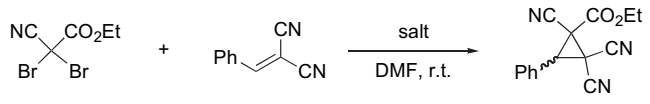
2b **3ab** 94% (2)

In this paper, we describe the reactions of various electron-deficient alkenes with activated dibromomethylene compounds by lithium iodide and tetrabutylammonium salts giving the corresponding cyclopropanes.

2. Results

The reactions of ethyl dibromocyanoacetate (**1a**) with benzylidene malononitrile (**2b**) were first examined by changing added salts. The results are summarized in Table 1. Without LiI no reaction proceeded and a catalytic amount of LiI was not enough to complete the reaction (entry 1). The reaction proceeded smoothly in the presence of a stoichiometric amount of LiI (entry 2). When LiBr or LiCl was employed, **1a** afforded **3ab** in moderate to good yields (entries 3 and 4). The use of NaI and KI resulted in similar results to the case of LiI (entries 5 and 6). KBr and KF also promoted the reaction, though

Table 1
Cyclopropanation of **2b** with **1a**[a]



1a **2b** **3ab**

Entry	Salt (mol %)	Time (h)	Yield[b] (%)
1	LiI (10)	24	9 (60:40)
2	LiI (100)	1	94 (51:49)
3	LiBr (100)	1	75 (69:31)
4	LiCl (100)	3	48 (73:27)
5	NaI (100)	1	82 (55:45)
6	KI (100)	1	95 (56:44)
7	KBr (100)	24	56 (67:33)
8	KF (100)	19	38 (64:36)
9	TBABr (100)	1	69 (56:44)
10	TBACl (100)	1	40 (92:8)
11	$Na_2S_2O_3$ (100)	2	50 (63:37)
12	KPF_6 (100)	23	13 (53:47)
13	$NaBF_4$ (100)	23	14 (53:47)
14	$LiClO_4$ (100)	21	6 (53:47)

[a] All reactions were carried out with **1a** (0.50 mmol), and **2b** (0.60 mmol) in DMF (1 mL).
[b] Values in parentheses refer to the diastereomeric ratio.

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a longer reaction time was requested (entries 7 and 8). Tetrabutylammonium bromide (TBABr) and tetrabutylammonium chloride (TBACl) were found to promote the reaction and the stereoselectivity was greatly increased in the latter case (entries 9 and 10). $Na_2S_2O_3$ gave a moderate yield (entry 11). KPF_6, $NaBF_4$, and $LiClO_4$ were not effective for this reaction (entries 12–14). These results indicate that halides salts, in particular, iodides are effective in increasing the reaction rate.

Next, solvent effects on the cyclopropanation were investigated (Table 2). The use of THF, acetone, and EtOH gave good results (entries 1–3). The reaction in CH_2Cl_2 for a longer time gave a moderate yield of **3ab** with a high level of the stereoselectivity (entry 4), whereas the use of diethyl ether resulted in an improvement of both the yield and the stereoselectivity (entry 5). The reaction in hexane gave a good stereoselection similar to that in diethyl ether, albeit the yield was moderate (entry 6). The poor yields in CH_2Cl_2 and hexane may come from the low solubility of LiI and **2b**.

Table 2
Solvent effects on the cyclopropanation of **2b** with **1a**[a]

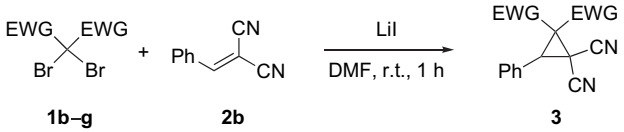
Entry	Solvent	Time (h)	Yield[b] (%)
1	THF	1	77 (57:43)
2	Acetone	1	82 (55:45)
3	EtOH	5	81 (58:42)
4	CH_2Cl_2	23	44 (91:9)
5	Et_2O	3	78 (92:8)
6	Hexane	20	45 (86:14)

[a] All reactions were carried out with **1a** (0.50 mmol), **2b** (0.60 mol) and LiI (0.50 mmol) in solvent (1 mL) at room temperature.
[b] Values in parentheses refer to the diastereomeric ratio.

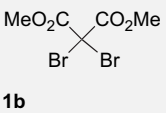
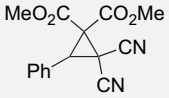
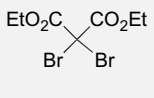
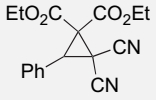
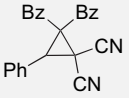
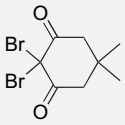
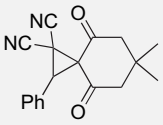
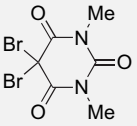
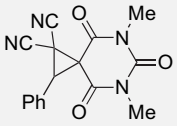
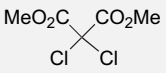
A series of dibromides **1b–f** was submitted to the cyclopropanation of **2b**. The results are summarized in Table 3. Dimethyl dibromomalonate (**1b**), diethyl dibromomalonate (**1c**), and dibromodibenzoylmethane (**1d**) gave cyclopropanes **3bb**, **3cb** and **3db**, respectively, in good to high yields (entries 1–3). When cyclic dibromides **1e** and **1f** were used, the corresponding spiro compounds were obtained (entries 4 and 5). Dichloride **1g** was proved to be less effective for this reaction (entry 6). Dibromodifluoromethane did not afford a coupling product.

The scope and limitation of alkenes for this cyclopropanation were examined by using **1a** (Table 4). The cyclopropanation of ethyl 2-cyanocinnamate (**2c**) in the presence of LiI afforded **3ac** in high yield (entry 1). In the case mediated by TBABr, **3ac** was obtained in

Table 3
Reactions of **2b** with various dibromides **1b–g**[a]

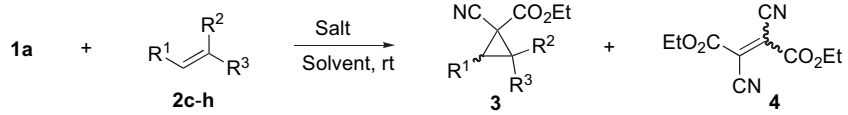


1b–g **2b** **3**

Entry	1	3	Yield (%)
1	 **1b**	 **3bb**	94
2	 **1c**	 **3cb**	89
3	 **1d**	 **3db**	74
4	 **1e**	 **3eb**	90
5	 **1f**	 **3fb**	72
6	 **1g**	**3bb**	8

[a] All reactions were carried out with **1** (0.50 mmol), **2b** (0.60 mmol) and LiI (0.50 mmol) in DMF (1 mL).

Table 4
Reactions of **1a** with various electron-deficient alkenes



2c-h **3** **4**

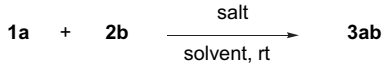
Entry	Conditions[a]	2	R^1	R^2	R^3	Time (h)	Yield of **3**[b] (%)	Yield of **4** (%)
1	**A**	**2c**	Ph	CN	CO_2Et	1	**3ac** 90 (47:53)	0
2	**B**	**2c**	Ph	CN	CO_2Et	5	**3ac** 31 (58:42)	0
3[c]	**B**	**2c**	Ph	CN	CO_2Et	5	**3ac** 43 (81:19)	0
4	**A**	**2d**	Ph	Ac	Ac	1	0	79
5	**A**	**2e**	Ph	Ac	CO_2Et	3	Trace	41
6	**A**	**2f**	Ph	CO_2Et	Ac	3	Trace	49
7	**A**	**2g**	Ph	CO_2Et	CO_2Et	1	Trace	83
8[d]	**A**	**2g**	Ph	CO_2Et	CO_2Et	1	**3ag** 24 (45:55)	63
9	**B**	**2g**	Ph	CO_2Et	CO_2Et	5	0	0
10	**A**	**2h**	Et	CN	CN	3	**3ah** 48 (50:50)	0
11	**B**	**2h**	Et	CN	CN	5	**3ah** 56 (59:41)	0

[a] Conditions **A**: the reactions were carried out with **1a** (0.50 mmol), **2** (0.60 mmol) and LiI (0.50 mmol) in DMF (1 mL) at room temperature. Conditions **B**: the reactions were carried out with **1a** (1.0 mmol), **2** (0.50 mmol) and TBABr (1.0 mmol) in THF (1 mL).
[b] Values in parentheses refer to the diastereomeric ratio.
[c] At reflux.
[d] **2g** (300 mol %) and LiI (200 mol %) were used.

lower yield, even though an excess amount of **1a** was used (entry 2). When the reaction temperature was elevated, the stereoselectivity was improved (entry 3). In contrast, **2d**–**g** were converted completely into a *cis*/*trans* mixture of dimer **4** in the presence of LiI (entries 4–7). When a larger amount of **2g** was used, the corresponding cyclopropane **3ag** was obtained in low yield together with dimer **4** (entry 8). In the case involving TBABr, neither the cyclopropane nor the dimer **4** was obtained (entry 9). The reactions of propylidenemalononitrile (**2h**) provide moderate yields of **3ah** in both the cases mediated by LiI and TBABr (entries 10 and 11). These results suggest that the presence of at least one strong electron-withdrawing group, such as a cyano group, is necessary for promoting the cyclopropanation. In the indium-mediated reactions,[3] ethyl acrylate and acrylonitrile gave the corresponding cyclopropanes upon the reactions of **1a**, whereas the InI_3-mediated reaction of acrylonitrile and **1a** without indium metal resulted in a dimerization of **1a** (42%). These facts clearly show that the nature of the intermediate in the present cyclopropanation is distinct from that in the indium-mediated reaction.

The reaction mediated by TBACl (entry 10, Table 1) or conducted in Et_2O (entry 5, Table 2) gave the excellent stereoselectivities, which promoted us to examine further optimization of the cyclopropanation (Table 5). The use of TBACl in diethyl ether afforded **3ab** with high stereoselectivity, though the yield was modest (entry 1). In contrast to the results with LiI (Table 2), TBACl showed a high level of the selectivity even in THF (entry 2). Increasing the amount of **1a** and TBACl led to an improvement in the yield (entries 3 and 4). TBABr was proved to be more effective than TBACl; less amount of TBABr was enough to finish the reaction keeping with a high level of the selectivity (entries 5 and 6).

Table 5
Reactions of **2b** with **1a** mediated by tetrabutylammonium salts[a]

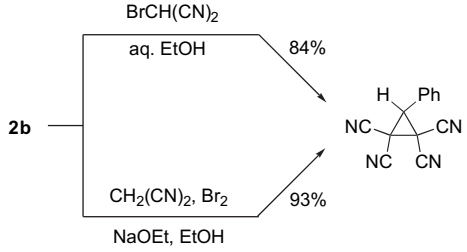


Entry	**1a** (mol %)	Salt (mol %)	Solvent	Time (h)	Yield[b]
1	83	TBACl (100)	Et_2O	1	32% (98:2)
2	83	TBACl (100)	THF	1	36% (98:2)
3	200	TBACl (200)	THF	3	65% (98:2)
4	300	TBACl (300)	THF	3	84% (98:2)
5	200	TBABr (200)	THF	3	84% (98:2)
6	300	TBABr (300)	THF	3	82% (98:2)

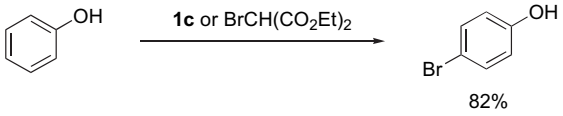
[a] The reactions were performed in solvent (1 mL) at room temperature.
[b] Values in parentheses refer to the diastereomeric ratio.

3. Discussion

Cyclopropanations of electron-deficient alkenes with bromomalononitrile[5] and malononitrile[6] have been documented, where bromomalononitrile is postulated as a common intermediate (Scheme 1). Diethyl dibromomalonate (**1c**) and diethyl bromomalonate were reported to be electrophilic brominating agents (Eq. 3), which release a bromonium ion. The presence of phenolic OH is



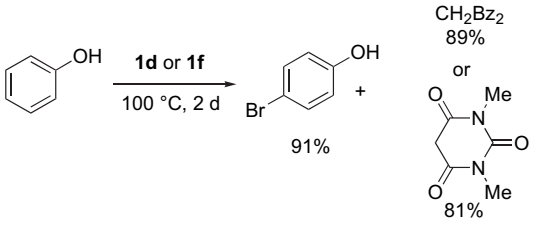
Scheme 1.



(3)

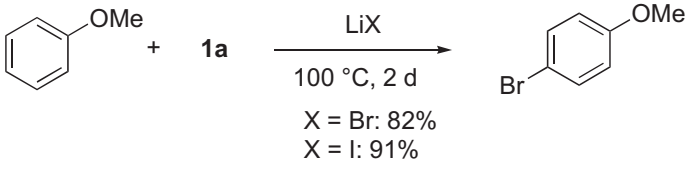
necessary to promote this bromination. Anisole persisted intact under the same conditions.[7]

In light of the above observations, we assumed that, the dibromides, of course including **1c**, also work as a brominating agent. Indeed, the reaction of dibromides **1d** and **1f** with phenol at 100 °C for two days, according to the conditions in the literature,[7] afforded *p*-bromophenol, along with dibenzoylmethane and barbituric acid, respectively. These facts indicate that **1d** and **1f** possess a similar capability of the bromination (Eq. 4).



(4)

Dibromides **1d** and **1f** may be protonated by the phenolic proton, which play a critical role to prevent a reverse reaction regenerating the dibromides. In the present cyclopropanation, lithium, or ammonium salts may play this role. To elucidate this possibility, we tested the bromination of anisole with **1a** in the presence of LiI, or LiBr at 100 °C for two days affording *p*-bromoanisole in good yields (Eq. 5).



(5)

The cyclopropanes **3ab**, **3ac**, **3ag** and **3ah** obtained in this work consisted of the *cis*/*trans* isomers, which are readily distinguishable by ^1H NMR (Fig. 1). The stereochemical assignments

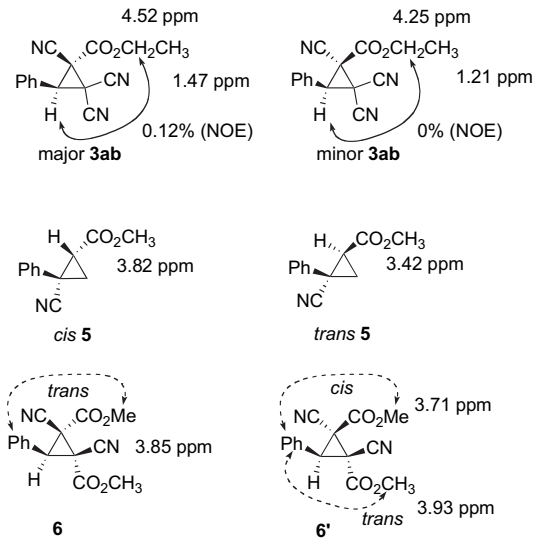
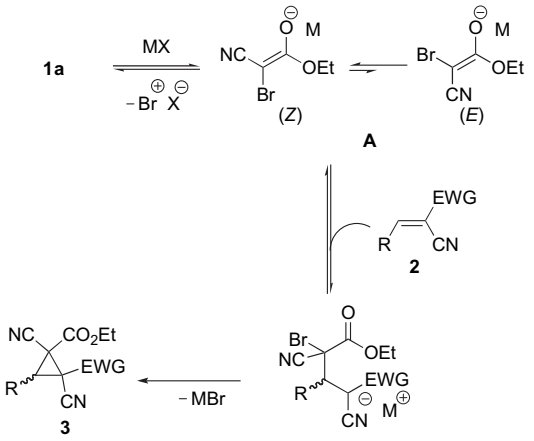


Figure 1.

were found on the comparison of known cyclopropanes **5**[8] and **6**,[9] where the methyl carboxylate group at the face opposite to that occupied by the phenyl group resonates at downfield compared to its *cis* counterpart. On the basis of these observations, the major isomer of **3ab** was determined to have a *trans* relationship between the phenyl group and the carboxylate group. This assignment was also confirmed by NOE experiments, showing an enhancement (0.12%) of the signal for the methylene protons upon irradiation of the benzylic proton in major **3ab** (Fig. 1). Similar assignments may be adapted to other products **3ac**, **3ag**, and **3ah**.

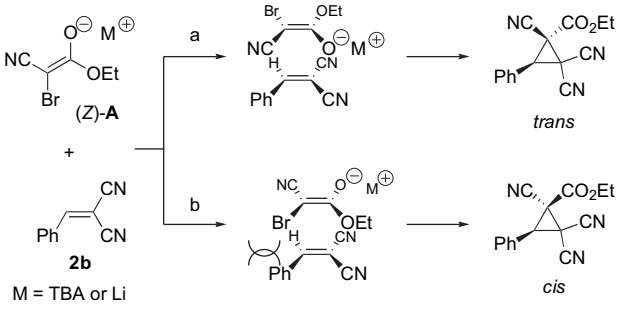
Taking into account the above results, a plausible reaction mechanism is proposed in Scheme 2. Dibromide **1** initially forms enolate **A** with releasing a bromonium ion, which is presumably



Scheme 2.

trapped by an iodide ion, or a bromide ion to prevent a recombination leading back to **1**. Enolate **A** undergoes a Michael addition to **2** affording cyclopropanes **3** via intramolecular cyclization.

The preferred formation of *trans*-**3** involving tetrabutylammonium salts can be rationalized in terms of structural circumstances during the transition state depicted in Scheme 3. The *Z* enolate, that may be favored over the *E* enolate due to a steric repulsion of the vinylic bromine and the anionic oxygen in **A**,[10] attacks **2** with a preference for the course *a* to avoid a steric hindrance between the bromine atom and the phenyl group. However, when the lithium salt and polar solvent were used, the drop-off in the level of the selectivity was observed (Tables 1 and



Scheme 3.

2). These results imply that the cationic counterpart marked in M is well solvated and serves as a sterically demanding group under these conditions, which cancel the preference of the course *a* over the course *b*.

4. Conclusion

The present study has revealed that, the treatment of active dibromomethylenes and electron-deficient alkenes with LiI, or tetrabutylammonium salts affords the corresponding cyclopropanes in high yields. The diastereoselectivity largely depends on the conditions. A proper choice of solvents and salts brings about success for enhancing yields and selectivities.

5. Experimental section

5.1. General

IR spectra were recorded on a JASCO FT/IR-200 spectrophotometer. ^{1}H NMR spectra were obtained for solutions in $CDCl_3$ on a Varian Gemini 200 spectrometer (200 MHz) with Me_4Si as internal standard. ^{13}C NMR spectra were measured for solutions in $CDCl_3$ with a Varian Gemini 200 spectrometer (50 MHz). Elemental analyses were done with a Perkin Elmer 2400II.

5.2. LiI mediated cyclopropanation of 2b with 1a (entry 2, Table 1)

To a mixture of **1a** (77 mg, 0.50 mmol) and LiI (67 mg, 0.50 mmol) in DMF (1 mL), **2b** (70 μL, 0.60 mmol) was added, and the mixture was stirred for 1 h. The product was extracted with Et_2O, washed with H_2O and brine, and dried over Na_2SO_4. The solvent was evaporated in vacuo and the product was purified by chromatography on SiO_2 (hexane–EtOAc=2:1, then EtOAc) affording **3ab** (124 mg, 94%, *dr*=51:49).

5.3. Ethyl 1,2,2-tricyano-3-phenylcyclopropanecarboxy-late[5a] (3ab)

^{1}H NMR (200 MHz, $CDCl_3$) δ 1.21 (t, J=7.2 Hz, 3H$_{cis}$), 1.47 (t, J=7.2 Hz, 3H$_{trans}$), 3.98 (s, 1H$_{cis}$), 4.04 (s, 1H$_{trans}$), 4.25 (q, J=7.2 Hz, 2H$_{cis}$), 4.52 (q, J=7.2 Hz, 2H$_{trans}$), 7.29–7.46 (m, 5H$_{cis}$), 7.50 (s, 5H$_{trans}$).

5.4. Dimethyl 2,2-dicyano-3-phenylcyclopropane-1,1-dicarboxylate[11] (3bb)

^{1}H NMR (200 MHz, $CDCl_3$) δ 3.77 (s, 3H), 3.96 (s, 4H), 7.30–7.44 (m, 5H).

5.5. Diethyl 2,2-dicyano-3-phenylcyclopropane-1,1-di-carboxylate[11] (3cb)

^{1}H NMR (200 MHz, $CDCl_3$) δ 1.19 (t, J=7.2 Hz, 3H), 1.39 (t, J=7.2 Hz, 3H), 3.95 (s, 1H), 4.23 (q, J=7.2 Hz, 2H), 4.32 (q, J=7.2 Hz, 2H), 7.35–7.40 (m, 5H).

5.6. 1,1-Dicyano-2,2-dibenzoyl-3-phenylcyclopropane (3db)

Colorless needles; Mp 167–168 °C (EtOH); IR (KBr) 3434, 3065, 2244, 1675, 1596, 1449, 1311, 1254, 1181, 1020, 764 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.38 (s, 1H), 7.20–7.64 (m, 7H), 7.68–7.77 (m, 2H), 7.98–8.08 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 16.5, 41.2, 56.0, 110.0, 112.3, 127.5, 128.4, 128.7, 128.9, 129.1, 129.4, 129.5, 133.7, 134.7, 135.1, 187.7, 188.0; Anal. Calcd for $C_{25}H_{16}N_2O_2$: C, 79.47; H, 4.15; N, 7.41. Found: C, 79.77; H, 4.28; N, 7.44.

5.7. 1,1-Dicyano-6,6-dimethyl-2-phenylspiro[2.5]-octane-4,8-dione (3eb)

Colorless plates; Mp 77–78 °C (EtOH); IR (KBr) 3597, 3406, 2968, 2874, 2249, 1702, 1447, 1375, 1309, 1224, 1046, 737, 698; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.21 (s, 6H), 2.68 (s, 1H), 2.71 (s, 1H), 2.83 (s, 2H), 4.12 (s, 1H), 7.1–7.2 (m, 2H), 7.3–7.4 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.1, 28.5, 29.0, 30.2, 44.3, 49.4, 53.2, 54.4, 109.5, 111.0, 127.1, 128.4, 128.8, 128.9, 195.9, 198.0; Anal. Calcd for $C_{18}H_{18}N_4O_2$+1/2·EtOH: C, 72.36, H, 6.07, N, 8.88. Found: C, 72.03, H, 6.23, N, 8.82.

5.8. 1,1-Dicyano-*N*,*N*-dimethyl-2-phenyl-5,7-diazaspiro-[2.5]octane-4,6,8-trione (3fb)

Colorless plates; Mp 219–220 °C (EtOH); IR (KBr) 3065, 2244, 1676, 1595, 1449, 1311, 1254, 1180, 1020, 938, 802, 763, 695, 595, 546; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.33 (s, 3H), 3.49 (s, 3H), 4.30 (s, 1H), 7.24–7.34 (m, 2H), 7.38–7.46 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.0, 29.7, 30.1, 40.9, 45.1, 108.8, 110.4, 126.1, 128.3, 129.0, 129.4, 149.5, 158.6, 161.3; Anal. Calcd for $C_{16}H_{12}N_4O_3$: C, 62.33; H, 3.92; N, 18.17. Found: C, 62.00; H, 3.71; N, 17.87.

5.9. TBABr mediated reactions of 1a with alkenes 2 (Table 4)

To a mixture of **1a** (154 mg, 1.0 mmol) and TBABr (322 mg, 1.0 mmol) in THF (1 mL), **2c** (100 mg, 0.50 mmol) was added, and the mixture was stirred for 5 h. The product was extracted with Et_2O, washed with H_2O and brine, and dried over Na_2SO_4. The solvent was evaporated, and the product was purified by chromatography on SiO_2 (hexane–EtOAc=2:1, then EtOAc) affording cyclopropane **3ac** (67 mg, 43%, *dr*=81:19).

5.10. Diethyl 1,2-dicyano-3-phenyl-1,2-cyclopropanedicarboxylate[9] (3ac)

^{1}H NMR (200 MHz, $CDCl_3$) δ 1.15 (t, J=7.1 Hz, 3H$_{trans}$), 1.36 (t, J=7.2 Hz, 6H$_{cis}$), 1.44 (t, J=7.1 Hz, 3H$_{trans}$), 3.93, (s, 1H$_{cis}$), 4.11 (s, 1H$_{trans}$), 4.18 (dq, J=2.9, 7.1 Hz, 2H$_{trans}$), 4.34 (q, J=7.2 Hz, 4H$_{cis}$), 4.42–4.51 (m, 2H$_{trans}$), 7.36 (s, 5H$_{cis}$), 7.42–7.47 (m, 5H$_{trans}$).

5.11. Diethyldicyanofumarate[12] (4)

^{1}H NMR (200 MHz, $CDCl_3$) δ 1.42 (t, J=7.2 Hz, 6H$_Z$), 1.46 (t, J=7.2 Hz, 6H$_E$), 4.46 (q, J=7.2 Hz, 4H$_Z$), 4.52 (q, J=7.2 Hz, 4H$_E$).

5.12. Triethyl 2-cyano-3-phenyl-1,1,2-cyclopropane-tricarboxylate[13] (3ag)

^{1}H NMR (200 MHz, $CDCl_3$) δ 1.06–1.42 (m, 9H), 3.93 (s, 1H$_{trans}$), 4.01 (s, 1H$_{cis}$), 4.08–4.41 (m, 6H), 7.27–7.40 (m, 5H).

5.13. Ethyl 1,2,2-tricyano-3-ethylcyclopropanecarboxyl-ate (3ah)

^{1}H NMR (200 MHz, $CDCl_3$) δ 1.15 (t, J=7.3 Hz, 3H$_{trans}$), 1.25 (t, J=7.3 Hz, 3H$_{cis}$), 1.38–1.45 (m, 3H), 1.87–2.04 (m, 2H), 2.70 (t, J=7.5 Hz, 1H$_{trans}$), 2.79 (t, J=7.5 Hz, 1H$_{cis}$), 4.36–4.49 (m, 2H).

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