Reaction of 1,1-Dichloro-2-(chloromethyl)cyclopropane with Some Carbanions: A Simple Synthesis of 1,2-Disubstituted Methylenecyclopropanes

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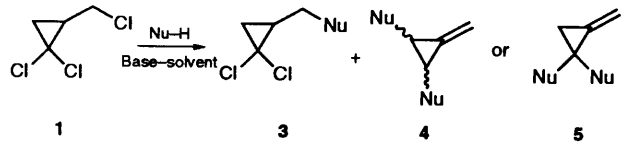
The reaction of cyclopropane **1** with 2-substituted phenylacetonitriles **2a–f** carried out in the presence of solid sodium hydroxide and benzyltriethylammonium chloride (TEBAC) as a catalyst in dimethyl sulfoxide, afforded 1,2-disubstituted methylenecyclopropanes **4a–f**. The chloride **1** reacted with phenylacetonitrile **2i** to give the chain-substituted product **3i**, while the reaction of **1** with diphenylacetonitrile **2h** gives a mixture of compounds **3h** and **4h**. The latter reaction carried out in conc. aq. NaOH–cat. TEBAC resulted in the formation of only the chain-substituted product **3h**. The nitriles **2** that contain a chiral centre formed a mixture of diastereoisomers of **4**.

Previously we have reported that the treatment of 1,1-dichloro-2-chloromethylcyclopropane **1** with carbanions from 2-phenylpropionitrile and diphenylacetonitrile [1] or heteroanions [1,2] (*e.g.* aryl oxides, alkoxides) leads to a unique transformation to afford 1,2- (**4**) or 1,1-disubstituted methylenecyclopropanes **5** along with the conventional products **3**. It has also been reported that the reaction of chloride **1** with some heteronucleophiles or sodium malonate gave products **3** [3] (Scheme 1).



Nu–H = ArCH(R)(CN)–H, ArO–H, RO–H

Scheme 1

Recently we have shown that a similar reactivity pattern is observed in the reactions of 1-bromo-2-(chloromethyl)cyclopropane with nucleophiles.[4]

Now, we report that the reaction of **1** with phenylacetonitriles substituted at C-2 (**2a–f**), carried out in the presence of powdered NaOH–cat. TEBAC in DMSO (System A), under mild conditions, is a convenient method for the preparation of the compounds **4a–f**, usually in good yields (Scheme 2, Table 1).

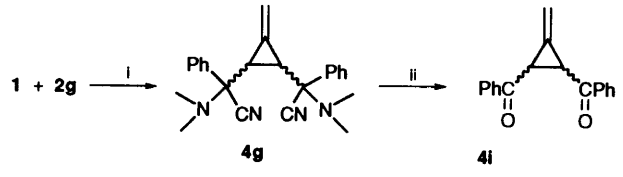
$$1 + \text{Nu–H} \xrightarrow[\text{system}]{\text{Base–solvent}} 3 \text{ and/or } 4$$

Scheme 2

Preliminary experiments with the nitriles **2d** and **2h** used in slight excess (**2**:**1** *ca.* 1.2) afforded the product **4d** and a mixture of **3h** and **4h**, respectively, in rather low yields (Table 1, Entries 4, 8). We also observed that the chloride **1** was almost completely consumed to form a tarry material. Therefore, further reactions of **1** with **2** were carried out with an excess of **2** (**2**:**1** *ca.* 3).

Our data reveal that the kind of product formed (**3** or **4**) depends on the structure of the carbanions generated from **2**. Carbanions formed by deprotonation of C–H acids possessing a reactive methylene group—**2i** in system A or **2j** in system C (solid potassium carbonate–DMF)—afforded chain-substituted products **3i** and **3j**, respectively. In the case of **2h**, the structure of the products was dependent on the base-solvent conditions: in system A both **3h** and **4h** were formed, while under phase transfer conditions (PTC) [5] in system D (50% aq. sodium hydroxide, TEBAC as catalyst), only product **3h** was isolated in a particularly low yield, accompanied by a significant amount of tarry material.

The reaction of **1** with amino nitrile **2f** using system A, led to the formation of the expected product **4f** which was fully characterized and then cleaved by $CuSO_4$–aq. EtOH to afford diketone **4i**. On the other hand, the reaction of **1** with **2g** did not give the corresponding methylenecyclopropane **4h** since $\mathbf{2g}^-$ was quickly oxidized to *N*,*N*-dimethylbenzamide. Indeed, such a base-mediated transformation of 2-(dialkylamino)phenylacetonitriles has already been described.[6] Therefore, the reaction of **1** with **2g** was performed in the presence of NaH in DMF (system B), and the crude **4g** was transformed into **4i** (Scheme 3). The reactions of **1** with amino nitriles **2f** and **2g**



Scheme 3 *Reagents and conditions:* i, NaH–DMF; ii, $CuSO_4$, EtOH–H_2O

proceeded with a relatively high rate in comparison with the other processes listed in Table 1.

The products **4** may exist as *trans* and *cis* isomers (with respect to the orientation of the two Nu groups on the cyclopropane ring). Furthermore, due to the four chiral centres, the presence of three diasteroisomers for each of *trans*-**4a–f** and *cis*-**4a–f** is expected. The statistical distribution of the diastereoisomers is 2:1:1, the major one for *trans*-**4** has *R* and *S* configurations of the Nu centres, while in *cis*-**4**, both the Nu centres have either *R* or *S* configuration. ^{1}H and ^{13}C NMR spectra (Tables 2 and 3) allowed us to elucidate the structures of the methylenecyclopropanes **4**. The spectral data indicate that the isolated products **4** never consisted of more than three diastereoisomers.

To assign the orientation of the substituents on the cyclopropane ring, a decoupling experiment (irradiation of the vinyl protons) on the predominant diastereoisomer of **4a**, **4d** (as a mixture of diastereoisomers) and **4f** was performed. It showed a simple AB system of cyclopropane protons in ^{1}H NMR spectra, and *J* 4.72, *J* 4.74 and *J* 4.36 Hz, respectively for **4a**, **4d** and **4f**, hence found are in fairly good agreement with *J* values for *trans* isomers of some other 1,2-disubstituted methylenecyclopropanes (J_{trans} 4.0–4.6, J_{cis} 9.6 Hz).[7] Taking into account

Table 1 Summary of the reaction conditions and products

Entry	Nu–H	Reaction conditions[a]			Method of isolation[c]	Products, yield (%)	
		Base–solvent system[b]	T/°C	t/h		**3**	**4**
1	**2a**, PhC(Me)(CN)–H	A	35	3	1		**4a**, 82
2	**2b**, PhC(Et)(CN)–H	A	20–25	5	1		**4b**, 81
3	**2c**, PhC($CH_2CH{=}CH_2$)(CN)–H	A	55–60	8	2		**4c**, 48
4	**2d**, PhC(CH_2Ph)(CN)–H	A	55–60	10	3		**4d**,[d] 59
5	**2e**, (4-C_5H_4N)CPh(CN)–H	A	54–58	10	1		**4e**, 24
6	**2f**, PhC[$NCH_2CH_2OCH_2CH_2$](CN)–H	A	20–25	0.25	3		**4f**, 68
7	**2g**, PhC(NMe_2)(CN)–H	B	20–25	0.25	4		**4g**, (32)[e]
8	**2h**, Ph_2C(CN)–H	A	40–45	5	3	**3h**,[f] 8	**4h**,[f] 66
9	**2i**, PhCH(CN)–H	A	20–25	1	5	**3i**, 51	
10	**2j**, ($MeO_2C)_2C$(H)–H	C	80	6	5	**3j**, 16	

[a] If not otherwise stated, the reactions were carried out with **2**:**1** (mol/mol) *ca.* 3. [b] A: solid NaOH–DMSO–cat. TEBAC; B: NaH–DMF; C: solid K_2CO_3–PhH-cat. TEBAC. [c] 1: excess of **2** was removed under reduced pressure, the product was vacuum distilled on Kugelrohr, and crystallized; 2: the product was isolated by CC, and vacuum distilled on Kugelrohr; 3: the product was isolated by crystallization; for isolation of **3h** and **4h**, see Experimental section; 4: the product was isolated by CC then crystallized; 5: the product was isolated by vacuum distillation. [d] With **2d**:**1** (mol/mol) *ca.* 1.2 (55–60 °C, 5 h), the yield of **4d** was 17%. [e] Pure **4g** was not isolated; this is the yield of diketone **4i**. [f] With **2h**:**1** (mol/mol) *ca.* 1.2 (55–60 °C, 3 h), the yields of **3h** and **4h** were 5 and 40%, respectively.

Table 2 ^{1}H NMR spectra (δ_H, $CDCl_3$, J/Hz) of compounds **4**

	Diastereoisomer	Ratio	Cyclopropane CH	C=CH_2	H in Nu
4a	I	3.7	1.91, 2.08 (m, 2 H, ^3J 4.72, ^4J 2.00, ^4J 2.48)	5.65, 5.79 (2 dd, 1 H each, ^4J 2.00, ^4J 2.48)	1.57, 1.75 (2 s, 3 H each, CH_3), 7.25–7.54 (m, 10 H, ArH)
	II	2	2.04 (t, 2 H, ^4J 2.26)	5.55 (t, 2 H, ^4J 2.26)	1.80 (s, 3 H, CH_3), 7.21–7.46 (m, ArH)
	III	1	1.99 (t, 2 H, ^4J 2.26)	5.84 (t, 2 H, ^4J 2.26)	1.68 (s, 3 H, CH_3), 7.21–7.46 (m, ArH)
4b	I	2.8		5.45, 5.70 (2 dd, 1 H each, ^4J 2.00)	0.98 (t, 6 H, J 7.3, CH_3CH_2)
			1.67–2.27 (m, collapsed with		7.14–7.50 (m, ArH)[a]
	II	1.4	CH_2 from Nu)[a]	5.33 (t, 2 H, ^4J 2.25)	0.66 (t, 6 H, J 7.3, CH_3CH_2)
	III	1		5.86 (t, 2 H, ^4J 2.25)	0.91 (t, 6 H, J 7.3, CH_3CH_2)
4c	I	2	2.02–2.05, 2.22–2.25 (m, 2 H)	5.48–5.50, 5.73–5.75 (m, 2 H)	2.35–2.52, 2.75–2.83 (2 m, 6 H each, CH_2=CHCH_2), 2.70 (dt, 6 H, ^3J 7.20, ^4J 1.05,
	II	1	2.13 (t, 2 H, ^4J 2.25)	5.38 (t, 2 H, ^4J 2.25)	CH_2=CHCH_2), 4.78–5.71 (m, 18 H,
	III	1	2.00 (t, 2 H, ^4J 2.28)	5.89 (t, 2 H, ^4J 2.28)	CH=CH_2), 7.16–7.56 (m, 30 H ArH)[a]
4d	I	10	2.06–2.15, 2.52–2.61 (m, 2 H)	5.05–5.10, 5.22–5.27 (m, 2 H)	2.85, 3.34 (2 s, 2 H each, CH_2Ph), 6.42–6.51, 7.00–7.64 (m, 20 H, ArH)
	II	1.2	2.12 (t, 2 H, ^4J 2.19)	5.05 (t, 2 H, ^4J 2.19)	3.16 (s, 2 H, CH_2Ph)
					Ar protons see notes[a,b]
	III	1	2.37 (t, 2 H, ^4J 2.20)	5.22 (t, 2 H, ^4J 2.20)	3.21 (m, 2 H, CH_2Ph)
					7.01–7.77 (m, 16 H, ArH and PyH)
4e	I	2		5.78 (t, ^4J 2.22)	8.56–8.66 (m, 2 H, PyH)
	II	1	2.97–3.07 (m, 2 H together)[a]	5.61 (t, ^4J 2.24)	
	III	1		5.70 (t, ^4J 2.17)	
				2 H together[a]	
4f	I	1.6	1.71–1.80, 2.14–2.20 (m, 2 H)	4.95 (t, 1 H, ^4J 2.20)	1.60–2.06 and 2.38–2.84 (2 m, 4 H each, CH_2NCH_2), 3.24–3.45 and 3.71–3.80 (2 m, 4
				5.33 (t, 1 H, ^4J 2.20)	H each, CH_2OCH_2), 7.26–7.68 (m, 10 H, ArH)
	II	1.2	1.74 (t, 2 H, ^4J 2.30)	5.22 (t, 2 H, ^4J 2.30)	2.39–2.95 (m, 8 H, CH_2NCH_2), 3.62–3.89 (m, 8 H, CH_2OCH_2), 7.26–7.35 (m, 10 H, ArH)
	III	1	1.87 (t, 2 H, ^4J 2.00)	5.87 (t, 2 H, ^4J 2.00)	2.25–2.72 (m, 8 H, CH_2NCH_2), 3.60–3.70 (m, 8 H, CH_2OCH_2), 6.95–7.20 (m, 10 H, ArH)

[a] Individual signals not assigned to the corresponding isomers. [b] The signals coincided with the signals of diastereoisomer I.

these data and the fact that the signals of only one geometrical isomer are present in the NMR spectra of the other products **4**, it is reasonable to postulate that compounds **4** have a *trans* structure.

We did not ascribe the *R* or *S* configurations of the carbon centres of a particular diastereoisomer on the basis of NMR spectra but for clarity the *trans* diastereoisomer with *R* and *S* configurations of the two quaternary carbon centres of Nu in **4** (see Scheme 2 and Table 1) was designated as I, and the diastereoisomer with both *R* (or *S*) and both *S* (or *R*) configurations as II and III, respectively. The spectra of the products **4** with different ratios of the isomers allowed us to

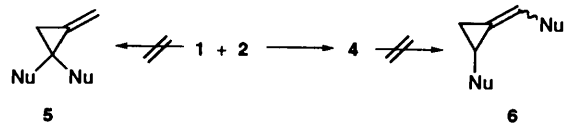
Table 3 ^{13}C NMR spectra (δ_C, $CDCl_3$) of compounds **4**

	Diastereoisomer	Cyclopropane CH	C=CH_2	C=CH_2	–$\overset{\vert}{C}$– in Nu	C≡N	C in R (R–C–Ph)	–$\overset{\vert}{C}$= in Ph	C–H in Ph
4a	I	25.65, 25.95	109.37	130.56	43.08, 43.17	121.09 121.26	28.76, 28.80 (CH_3)	139.25, 139.68	125.41, 125.60, 128.17, 128.29, 128.91, 129.07
	II + III	25.90, 26.09	109.36, 109.46	130.07, 130.62	42.87, 43.02	121.13, 121.41	29.17, 29.29 (CH_3)	138.76, 138.84	125.41, 125.74, 128.05, 128.26, 128.80, 128.91
4b	I + II	27.50, 28.66, 29.68	109.17	129.65, 130.70	49.73, 50.52	119.67, 119.98, 120.37	9.17, 9.65, 9.75 (CH_3); 32.60, 32.80, 33.00 (CH_2)	136.70, 137.39, 138.02	125.91, 126.12, 126.34, 127.99, 128.11, 128.26, 128.83, 129.11
	III	28.15	109.42	131.47	50.24	119.05	9.72 (CH_3), 35.54 (CH_2)	137.25	125.64, 127.77, 128.66, 129.00
4c	I–III	26.56, 27.52, 27.71, 29.01	109.32, 109.58, 109.99	129.17, 130.06, 130.68	43.63, 44.01, 44.28	119.05, 119.06, 119.46, 119.83	48.47, 48.56, 49.09, 49.45, (CH_2); 109.32, 109.58, 109.99 (=CH_2); 130.45, 130.88, 131.08 (=CH)	136.31, 136.77, 136.87, 137.55	125.53, 125.80, 126.03, 126.22, 127.70, 127.88, 127.99, 128.18, 128.43, 128.55, 128.86
4d	I	26.06, 28.88	109.38	130.37	50.56, 51.60	119.12, 119.70	46.56, 47.29 (CH_2Ph)	133.91, 134.46 136.88, 138.61	126.30, 126.73, 127.20, 127.47, 128.04, 128.48, 128.58, 129.09, 130.15, 130.45
	III	28.09	*a*	129.42	*a*	119.94	46.68 (CH_2Ph)	137.19	*a*
4e	I–III	26.91, 27.10, 27.31, 27.50	109.78, 110.07, 110.37	130.44, 130.51	55.81, 55.95, 56.02	119.32	136.80, 136.90, 137.07 (β-CH); 149.30, 149.48, 149.52, 149.55 (α-CH); 157.75, 157.81, 157.95, 158.04 (–C– in pyridyl)	138.40, 138.46, 138.78, 138.91	121.20–128.84
4f	I	25.83, 30.36	110.30	129.13	72.78, 73.39	113.76, 113.85	48.24, 48.86, (NCH_2), 66.61, 66.82 (OCH_2)	137.41, 137.71	125.76, 126.47, 126.70, 128.85, 129.53
	II	28.54	110.74	125.43	71.14	115.53	48.93 (NCH_2); 66.74 (OCH_2)	135.70	126.59, 128.73, 129.16
	III	25.82	110.24	131.88	73.39	114.01	48.86 (NCH_2); 66.81 (OCH_2)	136.20	125.75, 128.86, 128.99

[a] Due to small amount of *III*, the signals were not ascribed.

assign individual resonance signals for most of the diastereoisomers I–III of **4** (Tables 2 and 3). The crude products were purified before NMR spectra were measured to remove the tarry material. We cannot therefore reject the possibility that some of the products **4** had been lost and the ratio of diastereoisomers obtained changed. Some products **4** showed an almost statistical distribution of diastereoisomers I–III (ratio of *ca.* 2:1:1 determined by ^{1}H NMR), but in all cases diastereoisomer I prevailed, so we were able to isolate **I-4a** and **I-4f** in pure form.

Data from ^{1}H NMR as well as ^{13}C NMR spectra allowed us to eliminate an alternative 1,1-disubstituted structure **5** or the structure **6** (which may result from trimethylenemethane rearrangement[8]) for the products of the reaction of **1** with **2** (Scheme 4).



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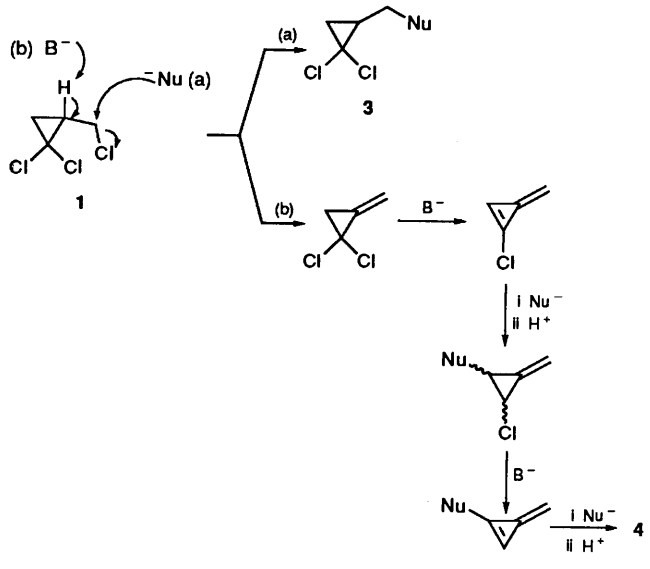
Scheme 4

It seems reasonable to assume that the products **3** are formed by simple nucleophilic substitution of a chlorine atom in the side chain of **1**, while methylenecyclopropanes **4** are formed *via* subsequent elimination–addition reactions. Such a mechanistic pathway has been supported experimentally for the reaction of **1** with phenolate anion, leading to **5** (Nu = PhO)[1] (Scheme 1). Location of the nucleophile at different carbon atoms in **4** serves as further support of this mechanism (Scheme 5).



Scheme 5

Methylenecyclopropenes have already been suggested as reactive intermediates in the reactions of nucleophiles with some 1-halogeno- and 1,1-dihalogeno-2-alkylidenecyclopropanes.[9]

To summarize, we have demonstrated that synthetically attractive methylenecyclopropane derivatives **4** can be simply synthesized from easily available substrates.

Experimental

M.p.s (recorded with a capillary tube apparatus) and b.p.s are uncorrected. NMR spectra were recorded on a Bruker-Spectrospin spectrometer (^{1}H 100 MHz and ^{13}C). Solutions in deuteriochloroform with tetramethylsilane as the internal standard were used. *J* Values are given in Hz. Microanalyses were performed on a Perkin-Elmer 240 CHN analyser. Column chromatography (CC) was carried out on Macherey Nagel silica gel 60 (70–270 mesh) with hexane–ethyl acetate as eluent; thin layer chromatography (TLC) on Merck precoated plates (silica gel 60 F_{254}, 0.2 mm). Dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) were distilled before use, sodium hydroxide was ground in a ball mill.

The following compounds were prepared by literature procedures: 1,1-dichloro-2-chloromethylcyclopropane **1** (52%), b.p. 58–60 °C/15 mmHg (lit.,[10] b.p. 57 °C/19 mmHg); 2-phenylpropionitrile **2a** (53%), b.p. 110–112 °C/11 mmHg (lit.,[11] b.p. 112–114 °C/13 mmHg); 2-phenylbutyronitrile **2b** (61%), b.p. 114–116 °C/14 mmHg (lit.,[11] b.p. 109–111 °C mmHg); 2-phenylpent-4-enenitrile **2c** (58%), b.p. 132–134 °C/14 mmHg (lit.,[11] b.p. 133–135 °C/14 mmHg); 2,3-diphenylpropionitrile **2d** (40%), m.p. 87–89 °C (lit.,[12] m.p. 87 °C); 2-(4-pyridyl)-2-phenylacetonitrile **2e** (46%), m.p. 74–76 °C (lit.,[13] m.p. 75–76.5 °C); 2-(morpholin-4-yl)-2-phenylacetonitrile **2f** (85%), m.p. 68–69 °C (lit.,[14] m.p. 69–70 °C); 2-(*N*,*N*-dimethylamino)-2-phenylacetonitrile **2g** (92%), b.p. 59–60 °C/0.3 mmHg (lit.,[15] b.p. 78–79 °C/1.1 mmHg). Commercial benzyltriethylammonium chloride (TEBAC) and C–H acids **2h–j** were used, the latter were crystallized or distilled before use. Sodium hydride Koch-Light Lab. (50% dispersion in oil; washed with benzene before use) was used.

A typical work-up consists of the extraction of the reaction mixture with chloroform (3 × *ca.* 80 cm^3 for 15–60 mmol-scale reaction), washing the combined organic extracts with water, drying ($MgSO_4$) and then evaporation of the solvent under reduced pressure.

General Procedure for the Synthesis of 1,2-*Disubstituted Methylenecyclopropanes* **4a–f**.—A mixture of DMSO (10 cm^3), powdered sodium hydroxide (2.4 g, 60 mmol), TEBAC (0.1 g, 0.44 mmol) and the nitrile **2a–f** (30 mmol) was stirred until the generation of heat ceased. Then a solution of **1** (1.59 g, 10 mmol) in DMSO (10 cm^3) was added and the reaction was stirred at the temperature and for the time indicated in Table 1. The mixture was poured into water, worked up and then the product was isolated by one of the methods 1–5 (Table 1).

1,2-*Bis*(1-*cyano*-1-*phenylethyl*)-3-*methylenecyclopropane* **4a**. An oil; b.p. 185 °C/0.1 mmHg (Kugelrohr), mixture of diastereoisomers I, II and III in the ratio of 3.7:2:1 (Found: C, 84.8; H, 6.3; N, 8.7. $C_{22}H_{20}N_2$ requires C, 84.6; H, 6.45; N, 9.0%). Crystallization of this oil from ethanol gave diastereoisomer I (46%), m.p. 95–96 °C (Found: C, 84.5; H, 6.45; N, 9.1). Attempted separation of II and III from the filtrate after crystallization of I, failed.

1,2-*Bis*(1-*cyano*-1-*phenylpropyl*)-3-*methylenecyclopropane* **4b**. Colourless oil; b.p. 145 °C/0.1 mmHg (Kugelrohr), mixture of diastereoisomers I, II and III (2.8:1.4:1) (Found: C, 84.7; H, 7.1; N, 8.05. $C_{24}H_{24}N_2$ requires C, 84.6; H, 7.1; N, 8.25%). Crystallization of this oil from ethanol afforded a mixture of isomers I and II (2:1), 63%, m.p. 86–87 °C (Found: C, 84.6; H, 7.1; N, 8.2).

1,2-*Bis*(1-*cyano*-1-*phenylbut*-3-*enyl*)-3-*methylenecyclopropane* **4c**. An oil; b.p. 210 °C/0.1 mmHg (Kugelrohr), mixture of diastereoisomers I, II and III (2:1:1) (Found: C, 85.45; H, 6.5; N, 7.4. $C_{26}H_{24}N_2$ requires C, 85.7; H, 6.6; N, 7.7%).

1,2-*Bis*(1-*cyano*-1,2-*diphenylethyl*)-3-*methylenecyclopropane* **4d**. Colourless crystals; m.p. 147–148 °C (from ethanol), mixture of diastereoisomers I, II and III (10:1:1.2) (Found: C, 88.0; H, 5.9; N, 6.2. $C_{34}H_{28}N_2$ requires C, 87.9; H, 6.1; N, 6.05%).

1,2-*Bis*[*cyano*(4-*pyridyl*)*phenylmethyl*] *methylenecyclopropane* **4e**. An oil; b.p. 180–210 °C/0.1 mmHg (Kugelrohr). After crystallization from ethanol a mixture of diastereoisomers I, II and III (2:1:1) in the form of colourless crystals (24%), m.p.

155–157 °C was obtained (Found: C, 81.95; H, 4.9; N, 13.2. $C_{30}H_{22}N_4$ requires C, 82.2; H, 5.1; N, 12.8%).

1,2-*Bis*[*cyanomorpholin*-4-*ylphenylmethyl*]-3-*methylenecyclopropane* **4f**. Colourless crystals; m.p. 152–215 °C (from hexane), mixture of diastereoisomers I, II and III (1.6:1.2:1). Fractional crystallization from hexane–cyclohexane allowed the isolation of pure isomers I and II. Isomer I, m.p. 205–206 °C (from ethanol) (Found: C, 73.8; H, 6.7; N, 12.5. $C_{28}H_{30}N_4O_2$ requires C, 74.0; H, 6.65; N, 12.3%). Isomer II, m.p. 160–162 °C (from hexane–cyclohexane) (Found C, 73.9; H, 6.7; N, 12.35%).

1,2-*Dibenzoyl*-3-*methylenecyclopropane* **4i**.—A mixture of DMF (10 cm^3), NaH (0.36 g, 15 mmol) and amino nitrile **2g** (2.40 g, 15 mmol) was stirred until the generation of heat ceased. Then a solution of **1** (0.80 g, 5 mmol) in DMF (2 cm^3) was added and the reaction mixture was stirred at 20–25 °C for 0.25 h and then diluted with water. The mixture was worked up, and the residue obtained was refluxed with $CuSO_4 \cdot 5H_2O$ (1.25 g, 5 mmol) in ethanol (10 cm^3) and water (15 cm^3) for 1 h. The solvent was evaporated off and the residue was diluted with water (50 cm^3) and extracted with chloroform (3 × 50 cm^3). The combined organic phases were washed with 10% aq. hydrochloric acid, then with water, dried ($MgSO_4$) and then concentrated. The product was isolated by CC to give the title compound **4i** (0.42 g, 32%), m.p. 59–60 °C (from MeOH) (Found: C, 82.2; H, 5.5. $C_{18}H_{14}O_2$ requires C, 82.4; H, 5.4%); δ_H 4.15 (2 H, t, *J* 2.45, cyclopropane CH), 5.58 (2 H, t, *J* 2.46, C=CH_2) and 7.49–7.63 and 8.06–8.15 (10 H, 2 m, 2 × Ar-H); δ_C 30.59 (cyclopropane CH), 103.83 (C=*C*H_2), 128.69, 128.78 and 133.57 (Ar CH), 133.14 (*C*=CH_2), 136.73 (Ar *C*–C=O) and 193.92 (C=O).

1,1-*Dichloro*-2-(2-*cyano*-2,2-*diphenylethyl*)*cyclopropane* **3h** *and* 1,2-*Bis*(*cyanodiphenylmethyl*)-3-*methylenecyclopropane* **4h**.—A mixture of DMSO (10 cm^3), powdered sodium hydroxide (2.4 g, 60 mmol), TEBAC (0.1 g, 0.44 mmol) and nitrile **2h** (5.8 g, 30 mmol) was stirred until generation of heat ceased. Then a solution of **1** (1.59 g, 10 mmol) in DMSO (10 cm^3) was added and the reaction mixture was stirred at 40–45 °C for 5 h. The mixture was poured into water, worked up and then the residue was crystallized from MeOH to give the title compound **4h** (2.88 g, 66%), m.p. 154–155 °C (Found: C, 87.85; H, 5.3; N, 6.4. $C_{32}H_{24}N_2$ requires C, 88.05; H, 5.5; N, 6.4%); δ_H 2.61 (2 H, t, ^4J 2.16, cyclopropane CH) 5.78 (2 H, t, *J* 2.20, C=CH_2) and 7.18 and 7.34 (20 H, 2 br s, 4 × Ar-H); δ_C 27.82 (cyclopropane-CH), 53.36 (–C–), 110.51 (C=*C*H_2), 119.67 (C≡N), 126.88, 127.50, 128.09, 128.28 and 128.84 (Ar-CH), 130.07 (*C*=CH_2) and 139.45 and 139.53 (Ar *C*).

The filtrate remaining after the crystallization of **4h** was diluted with chloroform (*ca.* 50 cm^3), washed with water, dried ($MgSO_4$), concentrated and then distilled at 220 °C/0.1 mmHg (Kugelrohr) to afford the title compound **3h** (0.25 g, 8%) as an oil (Found: C, 68.55; H, 4.65; N, 4.1; Cl, 22.7. $C_{18}H_{15}Cl_2N$ requires C, 68.35; H, 4.8; Cl, 22.4; N, 4.4%); δ_H 1.10–1.71 (3 H, m, cyclopropane CH and CH_2), 2.22–3.10 (2 H, m, CH_2) and 7.35–7.36 (10 H, m, 2 × Ar-H).

1,1-*Dichloro*-2-(2-*cyano*-2,2-*diphenylethyl*)*cyclopropane* **3h**.—A mixture of 50% aq. sodium hydroxide (25 cm^3), TEBAC (0.1 g, 0.44 mmol), the nitrile **2h** (11.6 g, 60 mmol) and chloride **1** (3.2 g, 20 mmol) was stirred under argon. After the generation of heat had ceased the reaction was stirred at 60 °C for 0.25 h (5 cm^3 of benzene was added to help the stirring of the semi-solid mixture) and then at 40 °C for 1 h. The mixture was diluted with water, worked up and after two distillations at b.p. 205 °C/0.1 mmHg (Kugelrohr) the product **3h** (0.54 g, 8.5%) was obtained as an oil.

1,1-*Dichloro*-2-(2-*cyano*-2-*phenylethyl*)*cyclopropane* **3i**.—A mixture of DMSO (10 cm^3), powdered NaOH (2.4 g, 60 mmol), TEBAC (0.1 g, 0.44 mmol) and the nitrile **2i** (3.51 g, 30 mmol) was stirred until the generation of heat ceased. Then a solution of chloride **1** (1.59 g, 10 mmol) in DMSO (10 cm^3) was added and the reaction was stirred at 20–25 °C for 1 h. The mixture was poured into water, worked up and then the residue was distilled (b.p. 104 °C/0.01 mmHg) to give the title compound **3i** (1.22 g, 51%) as an oil (Found: C, 60.45; H, 4.6; Cl, 29.15; N, 5.85. $C_{12}H_{11}Cl_2N$ requires C, 60.0; H, 4.6; Cl, 29.55; N, 5.85%); δ_H 1.13–1.88 (3 H, m, cyclopropane CH and CH_2), 1.95–2.37 (2 H, m, CH_2), 3.90–4.09 (1 H, m, CHCN) and 7.24–7.48 (5 H, m, Ar-H).

1,1-*Dichloro*-2-(2,2-*bismethoxycarbonylethyl*)*cyclopropane* **3j**.—A mixture of powdered potassium carbonate (6.21 g, 45 mmol), benzene (50 cm^3), TEBAC (0.15 g, 0.66 mmol), ester **2j** (1.98 g, 15 mmol) and chloride **1** (0.80 g, 5 mmol) was stirred under reflux (*ca.* 80 °C) for 6 h. The mixture was filtered and the solid was washed with benzene. The combined filtrate and washings were washed with water, dried ($MgSO_4$) and then concentrated. The residue was distilled (b.p. 130 °C/0.1 mmHg) to give the title compound **3j** (0.2 g, 16%) as an oil (Found: C, 42.65; H, 4.45; Cl, 27.6. $C_9H_{12}Cl_2O_4$ requires C, 42.45; H, 4.75; Cl, 27.8%); δ_H 1.13–1.27 (1 H, m, cyclopropane CH), 1.52–1.74 (2 H, m, cyclopropane CH_2), 2.09–2.24 (2 H, m, CH_2), 3.45–3.71 (1 H, m, CH) and 3.77 and 3.78 (total 6 H, 2 s, 2 × CH_3).

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