Phase-transfer catalysed (PTC) reactions of 1,1-dichloro-2-cyanocyclopropane with nucleophiles. Identification of intermediates

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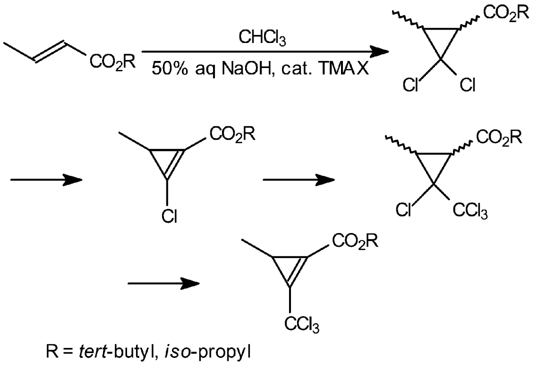
An addition–elimination mechanism for PTC reactions of phenols with 1,1-dichloro-2-cyanocyclopropane (**1**) is supported by trapping of intermediate cyclopropenes **3** and **5**. PTC reactions of **1** with a series of phenols **2a**–**d**, thiophenol (**2e**), alcohols **2f**,**g** and dithioles **11a**,**b** led to formation of disubstituted cyanocyclopropanes **6a**–**d**, **6e**, **6f**,**g** or spiroproducts **12a**,**b**, respectively. Under acidic conditions or thermally, dialkoxycyclopropanes **6f**,**g** or spirane **12a** were transformed into alkyl 3-cyanopropionates **10f**,**g** and ketene dithioacetal **13a**.

Substitution of halogen atoms by nucleophiles in *gem*-dihalocyclopropanes usually takes place according to elimination–addition mechanisms with participation of cyclopropene derivatives.[1] An electron-withdrawing group (EWG) facilitates this process which can be carried out by means of concentrated aqueous NaOH and a quaternary ammoniuim salt as a catalyst[2] (phase-transfer catalysis, PTC[3]). Substituted cyclopropenes have been isolated from the reaction of chloroform with *tert*-butyl-[4] as well as isopropyl crotonate,[5] carried out in the presence of 50% aq NaOH and tetramethylammonium salt (TMAX) as a catalyst (Scheme 1).

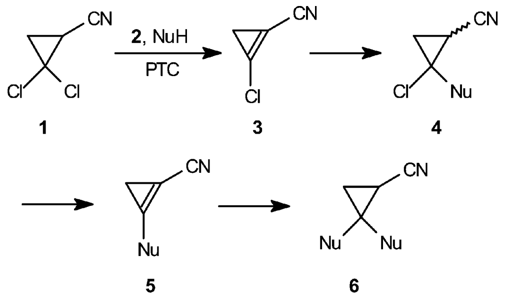
We report detailed results concerning the reactions of heteroanions generated under PTC conditions, with 1,1-dichloro-2-cyanocyclopropane (**1**). Base mediated transformations of nitrile **1** have been only briefly mentioned in the literature:[6] thiophenolate (generated from thiophenole by means of MeONa in MeOH) substitutes chlorine atoms in **1**, while alkoxides (MeONa or EtONa in the corresponding alcohols) cleave three-membered ring to form alkyl 3-cyanopropionates.

Results and discussion

The reaction of cyclopropane **1** with nucleophiles creates intermediates **3**–**5** (Scheme 2). Stirring of nitrile **1** with 2.2 equivalents of 4-chlorophenol (**2a**), 50% aq NaOH, and tetrabutylammonium bromide (TBABr) as a catalyst at temperature 35–40 °C for *ca.* 1 h led to the formation of **6a** and **4a** in *ca.* 2:1 ratio. The same reaction carried out with 1.1 equivalents of phenol **2a** afforded cyclopropanecarbonitrile **6a** as the main product (**6a**/**4a** *ca.* 23:1). Similarly, when irrespective of the **2a**/**1** ratio, this reaction was carried out at 20–25 °C, cyclopropane **6a** was again the main product.



Scheme 1



2,4-6	a	b	c	d	e	f	g
NuH	4-ClC$_6$H$_4$OH	4-O$_2$NC$_6$H$_4$OH	C$_6$H$_5$OH	4-MeC$_6$H$_4$OH	C$_6$H$_5$SH	MeOH	EtOH

Scheme 2

To prove the formation of cyclopropene **3** as a transient product leading to **4a**, we realized its trapping with 1,3-dienes **7**[9] (Scheme 3). Preliminary experiments which consisted of stirring nitrile **1** with an excess of diene **7a** in benzene, under PTC conditions with tetrabutylammonium hydrogen sulfate (TBAHS) as a catalyst, produced an intractable material. Possibly, the elimination of HCl from **1** (to give **3**) occurs at the phase boundary of a two-phase basic system where undesirable processes of **3** with HO$^-$ and/or water efficiently compete with the [4 + 2] cycloaddition. It seems, therefore, that generation of cyclopropene **3** by means of a lypophilic anion (*e.g.* quaternary ammonium phenolate) inside the organic phase, where the concentrations of HO$^-$ and water are negligible, should favour Diels–Alder product formation. It has been demonstrated that fairly weak O–H and N–H acids used as cocatalysts effectively promote the elimination of HBr from alkyl bromides under PTC conditions.[10] The experiment with cyclopropane **1**, an excess of diene **7a**, and a catalytic amount of phenol **2a** (**2a**/**1a** *ca.* 0.5), carried out under PTC conditions led to the

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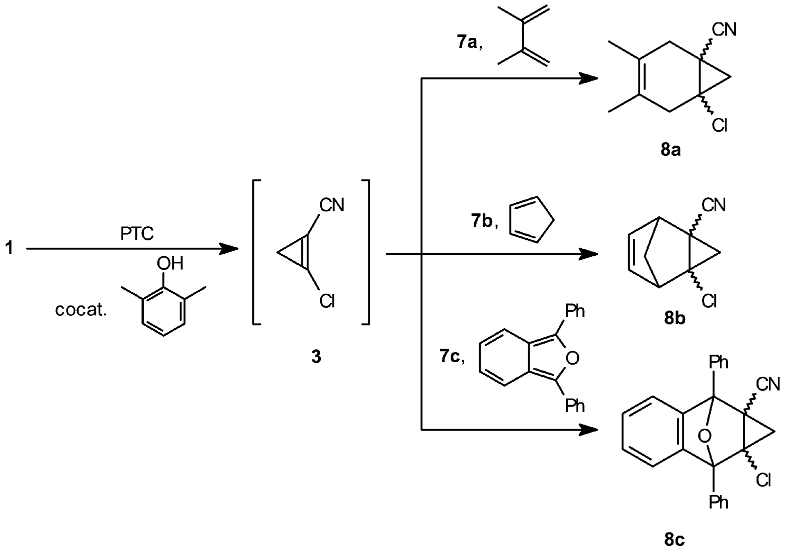


Scheme 3

formation of a mixture of nitrile **6a** and the expected adduct **8a**, rich in the former compound (**6a**/**8a** *ca.* 10). To supress undesired formation of the disubstituted product **6a**, the cocatalyst applied should eliminate HCl from **1** but should not add to cyclopropene **3**. These conditions were fulfilled by the sterically crowded 2,6-dimethylphenol as cocatalyst—the cycloadduct **8a** was isolated in 30–35% yield. Based on these observations, other adducts **8** were prepared in a similar manner (Scheme 3).

The presence of transient intermediate **5a** (Scheme 2) was proved indirectly by its trapping with 4-nitrophenolate (**2b**$^-$), PTC reaction of **4a** with 4-nitrophenol (**2b**) afforded 1-(4-chlorophenoxy)-1-(4-nitrophenoxy)-2-cyanocyclopropane (**9**), as a mixture of isomers. Therefore, the reaction pathway visualized in Scheme 2 is proved.

Stirring of nitrile **1** with 2.2 equivalents of phenol **2a**–**d**, thiophenol (**2e**) or an excess of alcohol **2f**,**g** in benzene, under PTC conditions (exothermic reactions), afforded products **6** in good yield (Scheme 2, Table 1). Dialkoxynitriles **6f**,**g** are unstable, and in the presence of mineral acid or during attempted purification by column chromatography on silica gel, they afforded alkyl 3-cyanopropionates **10f**,**g**. Similar properties have already been observed for nitrile **6f**,[7] and for 1,1-dialkoxycyclopropanes substituted by ethoxycarbonyl group.[11] Worth mentioning is the fact that PTC conditions, but not RO$^-$ in ROH,[6] allow the synthesis of *gem*-dialkoxy derivatives **6**.

With 1,2-ethane- (**11a**) and 1,3-propane-dithiol (**11b**), the corresponding spirodithioacetals of cyanocyclopropanone, **12a** and **12b**, were formed. A small amount of substituted ketene dithioacetal **13a** accompanied spiro compound **12a** (Scheme 4). The latter is thermally unstable and slowly forms **13a** during distillation. Benzoxazole derivative **14** was isolated in low yield from PTC reaction of nitrile **1** with 2-aminophenol. It is possibly produced *via* base-mediated cleavage of the intermediate spiro product as suggested for a similar reaction of 1,1-dihalophenylcyclopropanes with 2-aminoethanol, carried out by means of *t*-BuOK in DMSO.[12]

Table 1 1,1-Disubstituted-2-cyanocyclopropanes **6** prepared

6	Nu	Yield (%)	B.p. (°C/Torr) or m.p. (°C)
a	4-ClC_6H_4O	58	67–68 (MeOH)
b	4-$O_2NC_6H_4O$	65	140–141 (MeOH)
c	C_6H_5O	70	112–114 (MeOH)
d	4-MeC_6H_4O	80	200–210/1[a]
e	C_6H_5S	78	150–165/0.05[a b]
f	MeO	75	100/10[c]
g	EtO	80	60/0.6[d]

[a] Distillation on Kugelrohr apparatus. [b] Lit.[6] viscous liquid, isolated by column chromatography. [c] Lit.[7] identified by spectral method and lit.[8] distilled (b.p. 49–50 °C/2 Torr) and identified by IR spectra. [d] Lit.[8] distilled (b.p. 171–172 °C) and identified by IR spectra.

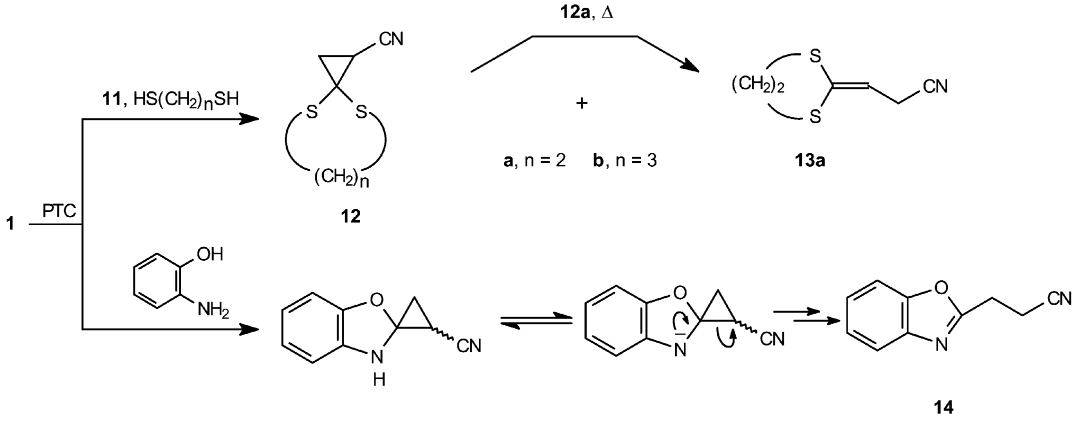
The results described above support the elimination–addition pathway for transformation of nitrile **1** into products **6**, **12** and **14**. These results also indicate that the reactions of phenols, thiols or alcohols with nitrile **1** can be conveniently carried out under PTC conditions.

Experimental

General

Melting points (measured with a capillary m.p. apparatus) and boiling points are uncorrected. ^1H NMR (400, 300, and 200 MHz) and ^{13}C NMR (100 and 50 MHz) spectra were measured on Varian equipment: Mercury-400BB, VXR-300 and Gemini-200BB respectively, as solutions in $CDCl_3$. GC analyses were performed on Hewlett-Packard 5890 Ser. II and Agilent Ser. 6850 chromatographs, equipped with HP50+ capillary columns (30 m). Elemental analyses were determined with a Perkin Elmer 2400 CHNO/S Ser. II microanalyser. Column chromatography was carried out on Merck Kieselgel 60 (230–400 mesh). 1,1-Dichloro-2-cyanocyclopropane (**1**) was prepared by the literature method.[6] Solvents and other reagents were commercial.

1-Chloro-1-(4-chlorophenoxy)-2-cyanocyclopropane (4a). A mixture of chlorophenol **2a** (1.41 g, 11 mmol), nitrile **1** (0.68 g, 5 mmol), TBABr (0.08 g, 0.25 mmol) and benzene (15 mL) was preheated to 32 °C and stirred vigorously while 50% aq NaOH (10.3 g, 7 mL, 130 mmol) was added dropwise during 15 min allowing the temperature to rise above 40 °C (exothermic effect). When the temperature dropped to 40 °C the mixture was stirred and maintained at this point for 30 min, then cooled and diluted with water (20 mL). After a typical work-up as described in the general procedure (see below), a sticky oil (containing **6a** and **4a** *ca.* 2:1 by GC) was obtained (*ca.* 1 g) which was distilled on a Kugelrohr apparatus collecting the fraction of b.p. 130–150 °C (oven)/0.1 Torr. Second



Scheme 4

distillation [b.p. 130–135 °C (oven)/0.15 Torr] gave 0.3 g (26%) of pure **4a** (99.4% by GC) as a mixture of stereoisomers in the proportion 11:1. ^{1}H NMR: (400 MHz) $\delta = 1.95$–2.05 (m, 2 H, CH_2), 2.23–2.28 (m, 1 H, CH), 7.01–7.05 and 7.30–7.34 (two m, 2 H each, arom. H). ^{13}C NMR: (100 MHz) (corresponding signal of minor isomer) $\delta = 15.35$ (15.77), 24.34 (24.48), 75.21 (74.70), 116.18 (115.43), 117.67 (117.96), 128.93, 129.67 (129.57), 152.54. Anal. calcd. for $C_{10}H_7Cl_2NO$:C, 52.66; H, 3.09; N, 6.14; Cl, 31.08; found C, 53.02; H, 3.04; N, 6.14; Cl, 31.11%.

1-(4-Chlorophenoxy)-1-(4-nitrophenoxy)-2-cyanocyclopropane (9). A mixture of nitrophenol **2b** (0.21 g, 1.5 mmol), cyclopropane **4a** (0.29 g, 1.27 mmol), TBABr (20 mg, 0.0625 mmol) and benzene (10 mL) was preheated to 30 °C and vigorously stirred while 50% aq NaOH (2.8 g, 2 mL, 35 mmol) was added dropwise within 5 min. The temperature of the mixture increased to 35 °C and was maintained during stirring for 2 h. After workup, the dark residue (containing **9**/**6a** *ca.* 15:1, by GC) was chromatographed over silica gel using ethyl acetate/hexane (1:4 v/v) to obtain 0.35 g (83%) of pure **9** (99.8% by GC) as a sticky oil (mixture of stereoisomers in comparable amounts). ^{1}H NMR: (400 MHz) $\delta = 1.93$–2.08 (m, 2 H, CH_2), 2.28–2.36 (m, 1 H, CH), 7.05–7.36 (m, 6 H, arom. H), 8.19–8.27 (m, 2 H, arom. H). ^{13}C NMR: (100 MHz) (corresponding signal of second isomer, ascribed on the basis of its slightly lower intensity) $\delta = 12.67$ (12.40), 20.37 (20.57), 86.40 (86.30), 115.76, 116.77 (116.92), 118.12 (117.83), 125.80 (125.73), 129.03 (128.95), 129.64 (129.73), 143.36 (143.44), 152.93 (152.87), 159.22 (159.26). Anal. calcd. for $C_{16}H_{11}ClN_2O_4$: C, 58.11; H, 3.35; N, 8.47; Cl, 10.72; found C, 58.34; H, 3.42; N, 8.29; Cl, 10.47%.

1,1-Disubstituted-2-cyanocyclopropanes 6a–e (General procedure). A mixture of phenol **2a**–**d** (22 mmol) or thiophenol (**2e**, 2.4 g, 22 mmol), nitrile **1** (1.36 g, 10 mmol), TBABr (0.16 g, 0.5 mmol) and benzene (30 mL) was vigorously stirred while 50% aq. NaOH (20 g, 13.5 mL, 250 mmol) was added dropwise at 25–30 °C (exothermic effect). When a temperature ceased, the mixture was stirred for 1.5–2 h, diluted with water (40 mL), the phases were separated, the water phase was extracted with benzene (3 × 15 mL), the combined organic extracts were washed with water (3 × 15 mL), and dried ($MgSO_4$). The solvent was evaporated, and the residue was crystallized from methanol or distilled on Kugelrohr apparatus (Table 1).

1,1-Di-4-chlorophenoxy-2-cyanocyclopropane (6a). Yield: 1.85 g (58%). ^{1}H NMR: (400 MHz) $\delta = 1.85$ (dd, $J = 6.8$ Hz, $J = 7.2$ Hz, 1 H, cyclopr. H), 1.95 (dd, $J = 6.8$ Hz, $J = 10.4$ Hz, 1 H, cyclopr. H), 2.19 (dd, $J = 7.2$ Hz, $J = 10.4$ Hz, 1 H, cyclopr. H), 7.06–7.09 (m, 2 H, arom. H), 7.13–7.16 (m, 2 H, arom. H), 7.27–7.31 (m, 4 H, arom. H). ^{13}C NMR: (100 MHz) $\delta = 12.63$, 20.64, 86.54, 116.23, 117.99, 118.31, 128.71, 128.80, 129.61, 129.71, 153.19, 153.29. Anal. calcd for $C_{16}H_{11}Cl_2NO_2$: C, 60.02; H, 3.46; N, 4.37; Cl, 22.14; found C, 60.08; H, 3.41; N, 4.36; Cl, 21.95%.

1,1-Di-4-nitrophenoxy-2-cyanocyclopropane (6b). Yield: 2.22 g (65%). ^{1}H NMR: (400 MHz) $\delta = 2.03$ (t, $J = 7.2$ Hz, 1 H, cyclopr. H), 2.12 (dd, $J = 7.2$ Hz, $J = 10.4$ Hz, 1 H, cyclopr. H), 2.40 (dd, $J = 7.2$ Hz, $J = 10.4$ Hz, 1 H, cyclopr. H), 7.25–7.40 (m, 4 H, arom. H), 8.22–8.26 (m, 4 H, arom. H). ^{13}C NMR: (100 MHz) $\delta = 12.63$, 20.51, 86.25, 115.32, 116.76, 116.94, 125.88, 125.95, 143.71, 143.79, 158.90, 158.93. Anal. calcd for $C_{16}H_{11}N_4O_2$: C, 56.31; H, 3.25; N, 12.31; found C, 56.27; H, 3.25; N, 12.13%.

1,1-Diphenoxy-2-cyanocyclopropane (6c). Yield: 1.75 g (70%). ^{1}H NMR: (400 MHz) $\delta = 1.85$ (t, $J = 6.8$ Hz, 1 H, cyclopr. H), 1.96 (dd, $J = 6.8$ Hz, $J = 10.4$ Hz, 1 H, cyclopr. H), 2.18 (dd, $J = 8.8$ Hz, $J = 10.4$ Hz, 1 H, cyclopr. H), 7.03–7.37 (m, 10 H, arom. H). ^{13}C NMR: (100 MHz) $\delta = 12.67$, 20.77, 86.18, 116.67, 116.69, 117.01, 123.26, 123.36, 129.52, 129.65, 154.84, 154.99. Anal. calcd for $C_{16}H_{13}NO_2$: C, 76.47; H, 5.21; N, 5.57; found: C, 76.57; H, 5.07; N, 5.46%.

Di-4-methylphenoxy-2-cyanocyclopropane (6d). Yield: 2.23 g (80%). ^{1}H NMR: (400 MHz) $\delta = 1.83$ (t, $J = 6.8$ Hz, 1 H, cyclopr. H), 1.92 (dd, $J = 6.8$ Hz, $J = 10.4$ Hz, 1 H, cyclopr. H), 2.16 (dd, $J = 6.8$ Hz, $J = 10.4$ Hz, 1 H, cyclopr. H), 2.35 (s, 6 H, CH_3), 7.09–7.19 (m, 8 H, arom. H). ^{13}C NMR: (100 MHz) $\delta = 20.39$, 20.43, 20.62, 86.45, 116.57, 116.77, 116.89, 129.85, 129.96, 132.57, 132.65, 152.66, 152.80. Anal. calcd for $C_{18}H_{17}NO_2$: C, 77.39; H, 6.13; N, 5.01; found C, 77.05; H, 6.02; N, 4.78%.

1,1-Diphenylthio-2-cyanocyclopropane (6e). Yield: 2.2 g (78%). ^{1}H NMR: (300 MHz) $\delta = 1.75$–2.10 (m, 3 H, cyclopr. H), 7.35–7.70 (m, 10 H, arom. H). Anal. calcd for $C_{16}H_{13}NS_2$: C, 67.80; H, 4.63; N, 4.94; found C, 67.60; H, 4.74; N, 4.78%.

1,1-Dialkoxy-2-cyanocyclopropanes 6f,g. Reaction of alcohols **2f,g** (70 mmol) with **1** was carried out as described in the general procedure (above). After the addition of alcohol the reaction mixture was worked up and the product was isolated by vacuum distillation. It was always accompanied by a small amount (3–5%) of the corresponding 3-cyanopropionate **10**, and the attempts to purify the product were unsuccessful. Satisfactory elemental analyses could not be obtained for cyclopropanes **6f,g**.

1,1-Dimethoxy-2-cyanocyclopropane (6f). Yield: 0.95 g (75%, purity 97% by GC). ^{1}H NMR: (400 MHz) $\delta = 1.45$–1.50 (m, 2 H, cyclopr. H), 1.73–1.78 (m, 1 H, cyclopr. H), 3.36 and 3.48 (two s, 3 H each, MeO). ^{13}C NMR: (100 MHz) $\delta = 11.06$, 20.12, 53.94, 53.97, 90.88, 117.88

1,1-Diethoxy-2-cyanocyclopropane (6g). Yield: 1.24 g (80%, purity 95% by GC). ^{1}H NMR: (400 MHz) $\delta = 1.20$ (t, $J = 7.2$ Hz, 3 H, CH_3), 1.28 (t, $J = 6.8$ Hz, 3 H, CH_3), 1.47–1.51 (m, 2 H, cyclopr. H), 1.74–1.78 (m, 1 H, cyclopr. H), 3.65–3.72 and 3.73–3.88 (parts AB of ABX_3, 2 H each, CH_2O). ^{13}C NMR: (100 MHz) $\delta = 11.35$, 14.97, 15.10, 20.47, 62.73, 62.97, 89.61, 118.28.

Alkoxycylopropanes **6f**,**g** were transformed into corresponding 3-cyanopropionates **10f**,**g** during attempted purification by column chromatography on silica gel (eluent: hexane/ethyl acetate 1:1).

Methyl 3-cyanopropionate (10f). ^{1}H NMR: (400 MHz) $\delta = 2.62$–2.72 (m, 4 H, CH_2CH_2), 3.74 (s, 3 H, CH_3O). ^{13}C NMR: (100 MHz) $\delta = 12.91$, 29.72, 52.34, 118.39, 170.46.

Ethyl 3-cyanopropionate (10g). ^{1}H NMR: (400 MHz) $\delta = 1.26$ (t, $J = 6.8$ Hz, 3 H, CH_3), 2.61–2.69 (m, 4 H, CH_2CH_2), 4.18 (q, $J = 6.8$ Hz, 2 H, CH_2O). ^{13}C NMR: (100 MHz) $\delta = 12.85$, 14.02, 29.87, 61.35, 118.45, 169.97.

Cyclic dithioacetals of 2-cyanocyclopropanone 12. The reaction was carried out as described in the general procedure using dithiol **11a**,**b** (11 mmol).

From **11a** the mixture of isomeric products **12a** and **13a** (*ca.* 24:1 by ^{1}H NMR, 0.74 g, 47%) was obtained, b.p. 96–97 °C/0.15 Torr.

2-Cyano-4,7-dithiaspiro[2,4]heptane (12a). ^{1}H NMR: (400 MHz) $\delta = 1.75$ (dd, $J = 6.4$ Hz, $J = 6.8$ Hz, 1 H, cyclopr. H), 1.84 (dd, $J = 6.8$ Hz, $J = 9.6$ Hz, 1 H, cyclopr. H), 1.91 (dd, $J = 6.4$ Hz, $J = 9.6$ Hz, 1 H, cyclopr. H), 3.40–3.51 (m, 4 H, dithiolane H). ^{13}C NMR: (100 MHz) $\delta = 17.39$, 17.93, 39.52, 39.57, 42.65, 118.05. Slow Kugelrohr distillation (b.p. 100 °C/0.15 Torr) increased the content of **13a** in the mixture (up to 25%, determined by ^{1}H NMR). This allowed to assign individual resonance signals for **13a**.

2-(2-Cyanoethylidene)-1,3-dithiolane (13a). ^{1}H NMR: (200 MHz) $\delta = 3.11$ (d, $J = 7.2$ Hz, 2 H, CH_2CN), 3.28–3.38 (m, 4 H, dithiolane H), 5.36 (t, $J = 7.2$ Hz, =CH). ^{13}C NMR: (50 MHz) $\delta = 20.17$, 37.51, 38.33, 42.59, 101.86, 117.07, 143.75. Anal. calcd for $C_6H_7NS_2$: C, 45.82; H, 4.50; N, 8.91; for the mixture of **12a**/**13a** (3:1) found: C, 45.90; H, 4.50; N, 9.02%.

2-Cyano-4,8-dithiaspiro[2,5]octane (12b). From **11b**, **12b** (0.89 g, 52%) was obtained, b.p. 102 °C/0.05 Torr. ^{1}H NMR: (400 MHz) $\delta = 1.57$–1.67 (m, 2 H, cyclopr. H), 2.02–2.06 (m, 1 H, cyclopr. H), 1.90–2.03 (m, 1H), 2.19–2.27 (m, 1H), 2.79–2.86 (m, 2 H), 3.01–3.08 (m, 1 H) and 3.13–3.20 (m, 1 H, all dithiane H). ^{13}C NMR: (100 MHz) $\delta = 19.10$, 23.93, 24.61, 29.78, 30.54, 31.79, 117.98. Anal. calcd for $C_7H_9NS_2$: C, 49.08; H, 5.31; N, 8.18; found C, 49.17; H, 5.26; N, 8.19%.

2-(2-Cyanoethyl)benzoxazole (14). The reaction was carried out as described in the general procedure, using 2-aminophenol (2.4 g, 22 mmol). The residue obtained after concentration of the benzene solution was passed through silica gel to remove tars. This allowed the crude product to be obtained (0.3 g, 17%, purity by GC > 92%). Analytical sample was obtained by sublimation *in vacuo* (80 °C/0.1 Torr), m.p. 86–88 °C. ^{1}H NMR: (200 MHz) $\delta = 2.94$–3.02 and 3.28–3.36 (two m, 2 H each, CH_2CH_2), 7.30–7.40 (m, 2 H, arom. H), 7.48–7.56 and 7.66–7.74 (two m, 1 H each, arom. H). ^{13}C NMR: (50 MHz) $\delta = 14.57$, 24.83, 110.57, 117.99, 119.77, 124.66, 125.35, 140.33, 150.77, 162.73. Anal. calcd for $C_{10}H_8N_2O$: C, 69.76; H, 4.68; N, 16.27; found: C, 69.60; H, 4.67; N, 16.30%.

Reaction of 1-chloro-2-cyanocyclopropene (3) with dienes 7a–c (General procedure). A mixture of nitrile **1** (1.36 g, 10 mmol), the corresponding 1,3-diene **7a**,**b** (30 mmol) or **7c** (10 mmol), 2,6-dimethylphenol (0.06 g, 0.5 mmol), TBAHS (0.035 g, 0.1 mmol) and benzene (5 mL) was stirred vigorously while 50% aq. NaOH (12 g, 8 mL, 150 mmol) was added dropwise during 15 min and cooled in order not to exceed 20 °C. The reaction mixture was stirred at this temperature for 2 h, and worked up in the usual way. The residue obtained after removal of the solvent was purified by column chromatography on silica gel using a mixture of hexane/ethyl acetate (gradient).

1-Chloro-6-cyano-3,4-dimethylbicyclo[4.1.0]hept-3-ene (8a). Yield: 0.64 g (35%), m.p. 47–49 °C (MeOH). ^{1}H NMR: (300 MHz) $\delta = 1.48$ and 1.54 (AB, $J = 6.2$ Hz, cyclopr. H), 1.58 and 1.59 (two s, 6 H together, 2 CH_3), 2.41–2.82 (m, 4 H, allyl CH_2). ^{13}C NMR: (50 MHz) $\delta = 18.50$, 18.54, 18.98, 22.49, 39.12, 44.27, 120.22, 120.58, 123.05. Anal. calcd for $C_{10}H_{12}ClN$: C, 66.12; H, 6.66; N, 7.71; Cl, 19.52; found: C, 65.97; H, 6.57; N, 7.57; Cl, 18.81%.

2-Chloro-4-cyanotricyclo[3.2.1.0^{2,4}]oct-6-ene (8b). Yield: 0.51 g (31%), oil. ^{1}H NMR: (200 MHz) $\delta = 1.89$ (m, 2 H, cyclopr. CH_2), 1.96–2.00 and 2.49–2.53 (two m, 1 H each, CH_2), 3.10–3.16 and 3.30–3.36 (two m, 1 H each, allyl CH), 5.96–6.02 and 6.14–6.20 (two m, 1 H each, vinyl CH). ^{13}C NMR: (50 MHz) $\delta = 21.62$, 35.67, 48.85, 52.58, 53.99, 62.06, 119.95, 133.38, 135.26. Anal. calcd for C_9H_8ClN: C, 65.30; H, 4.87; N, 8.46; Cl, 21.41; found: C, 65.51; H, 4.79; N, 8.46; Cl, 21.09%.

2-Chloro-4-cyano-1,5-diphenyl-8-oxabenzotricyclo[3,2,1,0^{2,4}]-oct-6-ene (8c). Yield: 1.11 g (30%), m.p. 137–138 °C. ^{1}H NMR: (200 MHz) $\delta = 2.39$ and 3.07 (two d, $J = 6.8$ Hz, 1H each, cyclopr. CH_2), 7.30–7.40, 7.48–7.55 and 7.72–7.80 (m, 14 H together, arom. H). ^{13}C NMR: (50 MHz) $\delta = 31.02$, 32.02, 58.06, 88.61, 90.64, 117.25, 121.36, 122.96, 127.27, 127.64, 127.97, 128.45, 128.72, 128.85, 129.56, 129.60, 131.80, 132.71, 145.97, 146.23. Anal. calcd for $C_{24}H_{16}ClNO$: C, 77.94; H, 4.36; N, 3.79; Cl, 9.58; found C, 77.70; H, 4.32; N, 3.74; Cl, 8.99%.

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