NH); MS (EI, m/e (relative intensity)) 705 (40, M + 1), 704 (100, M^+), 659 (8, M - NO_2^+), 612 (3, M - $2NO_2^+$), 352 (10, M^{2+} doubly charged); vis (λ_{max} in methylene chloride (log ϵ)) 420 (5.50), 516 (4.30), 551 (3.97), 5.92 (3.82), 646 (3.61). Anal. Calcd for $C_{44}H_{28}N_6O_4$: C, 74.99; H, 4.00; N, 11.92. Found: C, 74.66; H, 4.08; N, 11.30.

5-(4-Nitrophenyl)-10,15,20-tris(3-methylphenyl)porphyrin (5a). A stirred solution of 5,10,15,20-tetrakis(3-methylphenyl)-porphyrin (500 mg, 0.745 mmol) in 75 mL of chloroform was treated dropwise with yellow fuming nitric acid (1.60 g, 22.8 mmol, d = 1.50) over a 1.75-h period at 0-3 °C. The reaction medium was monitored by TLC, and when conversion of starting material (R_f = 0.83 in chloroform) to mononitro **5a** (R_f = 0.75) was noted, the medium was quenched with water and extracted as usual. Chromatography was conducted on a 2 in. × 18 in. silica column with chloroform as an eluent and afforded **5** (440 mg, 0.615 mmol) in 83% yield. An analytical sample was recrystallized by diffusion of hexane into a benzene solution of **5a**: IR ($CHCl_3$, cm^{-1}) 1603, 1518 (ν asymm NO_2), 1346 (ν symm NO_2), 805; ^1H NMR ($CDCl_3$) δ 8.90 (d, 2 H, J = 4.8 Hz, β-pyrrole), 8.87 (s, 4 H, β-pyrrole), 8.36 (d, 1 H), 8.21 (m, 2 H), 8.02 (m, 6 H), 7.61 (m, 6 H), 2.89 (s, 3 H), 2.64 (s, 9 H), -2.8 (s, 2 H, pyrrole NH); ^{13}C NMR ($CDCl_3$) δ 147.6, 141.9, 138.9, 136.2, 136.1, 135.5, 132.8, 131.9, 131.4, 129.6, 126.5, 123.1, 121.1, 120.7, 116.6, 21.7, 20.4; MS (EI, m/e (relative intensity)) 715 (100, M^+), 669 (8, M - NO_2^+), 358 (95, M^{2+} doubly charged). Anal. Calcd for $C_{48}H_{37}N_5O_2$: C, 80.54; H, 5.21; N, 9.78. Found: C, 80.21; H, 4.95; N, 10.20.

5,10-Bis(3-methyl-4-nitrophenyl)-15,20-bis(3-methylphenyl)porphyrin (5b). A second fraction (R_f = 0.63 *cis*-bis-**5b**:R_f = 0.68 *trans*-bis-**5b** in 3:1 ratio) was isolated from the chromatographic separation of **5a** in 9% yield (50 mg, 0.066 mmol): IR ($CDCl_3$, cm^{-1}) 3308, 1603, 1571, 1520 (ν sym NO_2), 1347 (ν asym NO_2), 853 (ν C-NO_2); ^1H NMR ($CDCl_3$) δ 8.91 (d, 2 H, J = 4.8 Hz), 8.88 (s, 2 H), 8.80 (s, 2 H), 8.76 (d, 2 H, J = 4.8 Hz), 8.34 (d, 2 H), 8.17 (m, 4 H), 8.01 (m, 4 H), 7.60 (m, 4 H), 2.88 (s, 6 H), 2.63 (s, 6 H), -2.79 (s, 2 H, NH pyrrole); ^{13}C NMR ($CDCl_3$) δ 151.9, 150.2, 144.6, 141.6, 139.2, 138.4, 135.7, 135.0, 134.9, 131.6, 129.6 126.0, 124.6, 120.1, 23.6, 23.6; MS (70 eV, EI) m/e (relative intensity) 760 (100, M^+), 715 (8, M - NO_2^+), 380 (79, M^{2+} doubly charged). An analytical sample was recrystallized by slow diffusion of hexane into a benzene solution of **5b**. Anal. Calcd for $C_{48}H_{36}N_6O_4$: C, 75.76; H, 4.77; N, 11.05. Found: C, 75.43; H, 4.30; N, 11.27.

5-(3-Methoxy-4-nitrophenyl)-10,15,20-tris(3-methoxyphenyl)porphyrin (6a). Yellow fuming nitric acid (1.21 g, 17.2 mmol) was added to a solution of *meso*-tetrakis(3-methoxyphenyl)porphyrin (500 mg, 0.745 mmol) in 75 mL of chloroform (0-3 °C). After the usual quench and workup procedure, the crude free base was applied to a 2 in. × 17 in. silica column and eluted with chloroform and then a 1:1 solution of chloroform in methylene chloride. An inseparable mixture of **6a** and its positional isomer (3-methoxy-6-nitrophenyl) **6b** was afforded in 55% yield (290 mg, 0.372 mmol, R_f = 0.32 for **6a**, **6b**; R_f = 0.45 for starting material in chloroform): IR ($CDCl_3$, cm^{-1}) 3320, 1600, 1520 (ν asym NO_2), 1352 (ν sym NO_2), 850 (ν C-NO_2); ^1H NMR ($CDCl_3$) δ 8.94 (d, 2 H, J = 4.8 Hz), 8.91 (s, 4 H), 8.80 (d, 2 H, J = 4.8 Hz) (d, 1 H, J = 14.3 Hz), 7.95 (d, 1 H, J = 1.5 Hz), 7.86 (dd, 1 H, J = 14.3, 1.5 Hz), 7.78 (m, 6 H), 7.60 (m, 3 H), 7.30 (m, 3 H), 4.02 (s, 3 H), 3.95 (s, H), -2.79 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 158.0, 151.2, 148.8, 143.2, 131.5, 127.6, 127.5, 126.6, 124.0, 120.7, 120.6, 120.5, 120.4, 120.1, 113.6, 113.5; MS (70 eV, EI) m/e (relative intensity) 779 (80, M^+), 734 (12, M - NO_2^+), 390 (100, M^{2+} doubly charged), 367 (32, M - NO_2^{2+} doubly charged). A closer inspection of the high field ^1H NMR spectrum revealed a 2:1 ratio of **6a**:**6b**. The following specific resonances were associated with **6b**: δ 8.65 (d, J = 4.8 Hz), 8.36 (d, J = 12.0 Hz), 7.66 (d, J = 1.8 Hz), 7.22 (d, J = 12.0 Hz), 3.87 (s), -2.70 (s). Anal. Calcd for $C_{48}H_{37}N_5O_6$: C, 73.91; H, 4.79; N, 8.98. Found: C, 73.5; H, 5.03; N, 9.10.

Registry No. **1a**, 67605-65-6; **1b**, 67605-64-5; **2a** (M = Na^+), 39050-26-5; **2b** (M = NH_4^+), 68438-24-4; *trans*-**3**, 79109-32-3; *cis*-**3**, 79109-31-2; **4a**, 116430-09-2; **4b**, 116206-77-0; **5a**, 119695-92-0; *cis*-**5b**, 119720-85-3; *trans*-**5b**, 119720-86-4; **6a**, 119695-93-1; **6b**, 119695-94-2; *meso*-tetraphenylporphyrin, 917-23-7; *meso*-tetrakis(3-methoxyphenyl)porphyrin, 29114-93-0; 5,10,15,20-tetrakis(3-methylphenyl)porphyrin, 50849-45-1.

A New Reaction of 1-Bromo-2-(chloromethyl)cyclopropane in Basic Medium: A Simple Preparation of 1-(Alkoxymethylene)cyclopropanes[1]

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A study of the recent literature reveals a still growing interest in chemical transformations of 1-halo- or 1,1-dihalo-2-(halomethyl)cyclopropanes. Thus the compounds **1a** or **1** (X = Y = Br; Z = Cl) treated with magnesium, sodium, or lithium alkyls afforded bicyclobutanes **2** (Y = H)[2-4] or **2** (Y = Br),[5-7] respectively. A derivative of **1** (X = Y = Br; Z = Cl; R^1 = CH_2Cl) served as a convenient source of the strained [1.1.1]propellane (**3**), which was formed via **2**.[8] The compounds **2** and **3** were usually accompanied by variable amounts of other products. Compounds **1** (X = Y = Br; Z = Cl, OMs) underwent $Ni(CO)_4$-induced ring-opening carbonylation reactions with alcohols and amines leading to derivatives of γ,δ-unsaturated carboxylic acids **4**.[9]

On the other hand, the chain bromine atom in the *gem*-dichloro derivative of **1** (X = Y = Cl; Z = Br) was easily substituted by nucleophiles affording **5**.[10] We have found[11] the reactivity pattern of the above mentioned compound **1** to be strongly influenced by the nature of nucleophilic reagent and reaction conditions, leading to the formation of **5** and/or its mixture with methylenecyclopropane derivatives **6a,b** (Scheme I). It has been proved that **6** is produced via a series of elimination-addition reactions.

On the basis of our own results[11] and literature data[12] we expected that the reaction of **1a** with nucleophiles would afford either 1-substituted methylenecyclopropanes and/or chain substituted products.

Indeed we have found that simple stirring of **1a** with an excess of alcohols **7a-f**, in the presence of powdered sodium hydroxide and triethylbenzylammonium chloride (TEBACl) as a catalyst, in DMSO, at ambient temperature during the time indicated in Table I, gives rise to the expected 1-(alkoxymethylene)cyclopropanes **8a-f**, usually in high yields. Alcohols of different structure including aliphatic, alicyclic, as well as substituted by an aryl or heterocyclic group entered this reaction (table). On the other hand, phenols **7g-i**, thiophenol (**7j**), and nitriles **7k,l** gave the chain-substituted products **9g-l**. In these cases the formation of methylenecyclopropane derivatives **8** was not observed (by ^1H NMR spectra of the crude reaction

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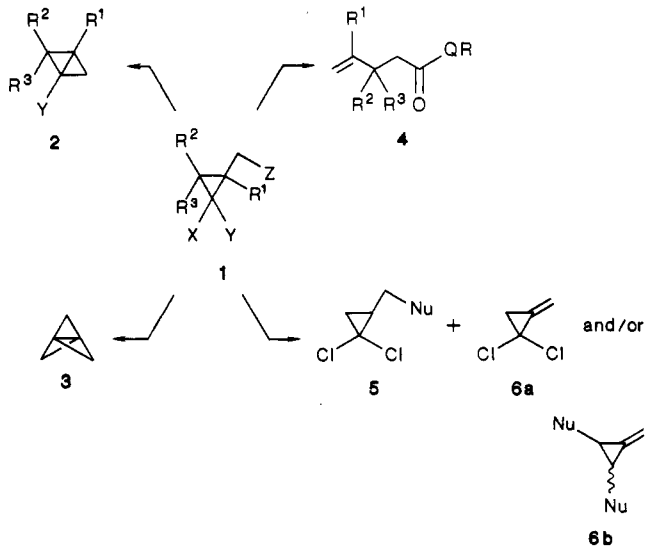
Table I. Products 8 and 9 from the Reaction of 1a with 7

1a 7 8 9

entry	R–H	base/solvent system[a]	ratio of 7/1a, mol/mol	reaction time, h	products: method of isolation[b]	products: 8, % yield	products: 9, % yield
1	**7a**, $CH_3(CH_2)_2CH_2OH$	A	3.0	8	I	**8a**, 64	
2	**7b**, $CH_3(CH_2)_4CH_2OH$	A	3.0	8	II	**8b**, 81	
3	**7c**, $CH_3(CH_2)_8CH_2OH$	A	3.0	10	II	**8c**, 81	
4	**7d**, c-$C_6H_{11}OH$	A	1.2	10	I	**8d**, 94	
5	**7e**, $C_6H_5CH_2OH$	A	3.0	2	I	**8e**, 75	
6	**7f**, 2-thienyl CH_2OH	A	1.2	8	II	**8f**, 73	
7	**7g**, C_6H_5OH	A	3.0	8	III		**9g**, 81
8	**7h**, 4-ClC_6H_4OH	A	3.0	8	I		**9h**, 46
9	**7i**, 4-$CH_3OC_6H_4OH$	A	3.0	8	I		**9i**, 58
10	**7j**, C_6H_5SH	A	1.2	2	III		**9j**, 62
11	**7k**, $C_6H_5C(CH_3)(CN)H$	A	3.0	5	IV		**9k**, 56
12	**7l**, $C_6H_5C(CH_2C_6H_5)(CN)H$	A	3.0	5	V		**9l**, 78
13	**7m**, $(C_6H_5)_2C(CN)H$	A[c]	1.2	6	VI	**8m**, 41	**9m**, 8
14	**7n**, $C_6H_5CH(CN)H$	B[d]	1.2	5	IV		**9n**, 48
15	**7o**, $(CH_3OOC)_2CH_2$	C	1.2	5	III		**9o**, 45

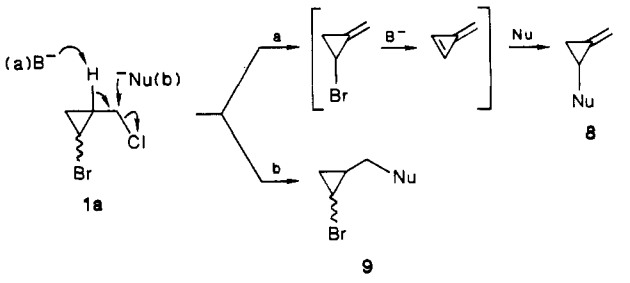
[a] A: solid NaOH/DMSO/catalytic TEBACl. B: NaH/DMSO. C: solid K_2CO_3/C_6H_6/catalytic TBABr. [b] I: the product was isolated by CC. II: the product was isolated by CC and then vacuum distilled on Kugelrohr. III: the product was isolated by vacuum distillation. IV: the excess of 7 was removed by vacuum distillation and the residue was purified by CC. V: unreacted 7 was removed by means of isopropyl-3-chloropropionate,[13] the product was vacuum distilled on Kugelrohr. VI: the product was isolated by CC and crystallized. [c] In the system B only **9m** (yield 55%) was isolated. [d] In the system A tarry material was formed.

Scheme I



usually: R^1, R^2, R^3 = H, Me RQH: ROH, RNH_2, R_2NH
X = H; X, Y, Z = Cl, Br; Z = OMs NuH: C—H, O—H, S—H acids
1a: $R^1 = R^2 = R^3$ = H; X = H; Y = Br; Z = Cl

Scheme II



mixtures). Diphenylacetonitrile (**7m**) is the only C–H acid whose anion, generated under the above cited conditions, in reaction with **1a** afforded a mixture of two products (**8m** and **9m**), whereas in a NaH/DMSO system it produced exclusively **9m**. The latter system was succesfully applied in the synthesis of **9n** from **7n** and **1a**. Since methyl esters of carboxylic acids are easily hydrolyzed by aqueous sodium hydroxide, methyl malonate (**7o**) was allowed to react with **1a** in the presence of solid potassium carbonate and tetrabutylammonium bromide (TBABr) as a catalyst, in benzene (solid–liquid catalytic two-phase system[14]) to afford **9o**.

The starting cyclopropane **1a** was synthesized[3] as a mixture of *Z* and *E* isomers (55:45); all products **9** consisted of a mixture of *Z* and *E* isomers, of similar ratio (GLC data).

Considering the literature[12] and our own data[11] concerning base-induced transformations of trihalo derivatives **1**, it seems reasonable to assume that products **8** are formed via subsequent elimination–addition reactions, while products **9** are produced via a simple nucleophilic substitution of a chlorine atom in the side chain of **1a** (Scheme II). Therefore both, base and nucleophile are needed for the formation of **8**. In the NaOH/DMSO/catalytic TEBACl system, OH^- as well as 7^- may act as base. Since this system is in fact a two-phase system,[15] in which the interfacial phenomena may play an important role and since the concentration of anions 7^- in organic phase depends on pK_a of the applied acid **7**, it is difficult to state whether 7^-, OH^-, or both act as base.

To the best of our knowledge, products **8**—except **8**, R = O-*t*-Bu and SO_nMe (n = 0, 2)[12]—are not described in the literature. Structurally related 1-alkylidene-2-alkoxycyclopropanes are available[16,17] via reaction of vinyl

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ethers with alkylidenecarbenes generated under PTC[18,19] conditions.

Structural assignments for **8** and **9** were made on the basis of physical and spectral data (see the Experimental Section).

To conclude, we have presented a new, convenient route for preparation of compounds **8**, based on easily available starting materials. Attempts are being made to apply this approach to the synthesis of some natural products derived from methylenecyclopropane.[20]

Experimental Section

Infrared spectra were measured as liquid films or in KBr pellets on a Specord 75 IR Carl-Zeiss Jena spectrophotometer. Nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 100 MHz (Bruker-Spectrospin spectrometer) in $CDCl_3$ solution. Chemical shifts (δ) are given in ppm relative to TMS internal standard. Mass spectra were recorded on a LKB 2091 spectrometer. GLC analyses were carried out on a Chromatron gas chromatograph GCHF 18.3 using an OV 17 column (5% silicon oil OV-17 on Chromosorb W) and flame-ionization detector with nitrogen as carrier gas. Column chromatography (CC) was conducted with Merck silica gel MN-60 (70–270 mesh ASTM) and hexane–ethyl acetate as eluent. Melting points and boiling points are uncorrected. DMSO was distilled before use. NaOH was ground on a ball mill. The starting cyclopropane **1a** was prepared by the literature procedure[3] from **1** (X = Y = Br; Z = Cl), which in turn was synthesized from allyl chloride and bromoform in a catalytic two-phase system, with tributylamine as the catalyst.[21]

The Products 8a–f,m and 9g–m from the Reactions of 1a with 7a–m in Solid NaOH/DMSO/Catalytic TEBACl System. DMSO (5 mL), powdered NaOH (1.2 g, 30 mmol), TEBACl (0.05 g, 0.22 mmol), and the corresponding O–H, S–H, or C–H acid (Table I) were stirred until the thermal effect ceased. Then the solution of **1a** (0.85 g, 5 mmol) in DMSO (5 mL) was added, and the reaction was heated at 56–58 °C for the time indicated in the table. The mixture was poured into water and extracted with CH_2Cl_2 or $CHCl_3$ (3 × 100 mL). The organic extracts were washed with water, dried ($MgSO_4$), and concentrated on a rotary evaporator. The residue was worked up by one of the methods I–VI (Table I).

8a: oil; ^{1}H NMR δ 0.85–0.98 (m, 3 H, CH_3), 1.13–1.73 (m, 6 H, CH_2CH_2 and CH_2 of cyclopropane ring), 3.32–3.74 (m, 3 H, OCH_2 and CH of cyclopropane ring), 5.49–5.69 and 5.71–5.74 (2 m, 2 H, C=CH_2). Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.96; H, 11.05.

8b: oil; bp 87 °C (10 mm); ^{1}H NMR δ 0.88–0.98 (m, 3 H, CH_3), 1.07–1.63 (m, 10 H, $(CH_2)_4$ and CH_2 of cyclopropane ring), 3.33–3.74 (m, 3 H, OCH_2 and CH of cyclopropane ring), 5.48–5.69 and 5.71–5.74 (2 m, 2 H, C=CH_2). Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.56; H, 11.50.

8c: oil; bp 98 °C (0.05 mm) (Kugelrohr); ^{1}H NMR δ 0.81–0.93 (m, 3 H, CH_3), 1.26–1.57 (m, 18 H, $(CH_2)_8$ and CH_2 of cyclopropane ring), 3.47–3.60 and 3.63–3.75 (m, 3 H, OCH_2 and CH of cyclopropane ring), 5.46–5.52 and 5.67–5.74 (2 m, 2 H, C=CH_2). Anal. Calcd for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 79.89; H, 12.51.

8d: oil; ^{1}H NMR δ 1.17–2.08 (m, 12 H, $(CH_2)_5$ and CH_2 of cyclopropane ring), 3.38–3.81 (m, 2 H, CH of cyclopropane ring and CH of cyclohexane ring), 5.47–5.53 and 5.65–5.73 (2 m, 2 H, C=CH_2). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.99; H, 10.75.

8e: oil; ^{1}H NMR δ 1.32–1.40 (m, 2 H, CH_2 of cyclopropane ring), 3.71–3.83 (m, 1 H, CH of cyclopropane ring), 4.60 (s, 2 H, OCH_2), 5.46–5.53 and 5.64–5.71 (2 m, 2 H, C=CH_2), 7.24–7.35 (m, 5 H, aromatic H); MS m/e (relative intensity) 131 (M – CHO, 7), 107 (12), 91 ($C_7H_8^+$, 100), 83 (3), 78 (6), 77 (6), 69 (4), 41 (5), 28 (6). Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.51; H, 7.50.

8f: oil; bp 70 °C (0.05 mm) (Kugelrohr); ^{1}H NMR δ 1.25–1.42 (m, 2 H, CH_2 of cyclopropane ring), 3.73–3.85 (m, 1 H, CH of cyclopropane ring), 4.75 (s, 2 H, OCH_2), 5.47–5.53 and 5.64–5.71 (2 m, 2 H, C=CH_2), 6.92–7.06 and 7.24–7.31 (m, 3 H, H of thiophene ring); MS m/e (relative intensity) 166 (M^+, 1), 137 (M – CHO, 6), 97 (100), 53 (8), 45 (12). Anal. Calcd for $C_9H_{10}OS$: C, 65.02; H, 6.06; S, 19.29. Found: C, 65.19; H, 6.09; S, 19.69.

9g: oil; bp 80 °C (0.05 mm); ^{1}H NMR δ 0.80–1.79 (m, 3 H, CH_2 and CH of cyclopropane ring), 2.80–3.26 (m, 1 H, CH of cyclopropane ring), 3.68–4.19 (m, 2 H, OCH_2), 6.71–7.45 (m, 5 H, aromatic H); IR (film) 3060–3040, 2930–2870, 1590, 1490, 1405, 1240, 1180, 1080, 750, 700 cm^{-1}. Anal. Calcd for $C_{10}H_{11}BrO$: C, 52.89; H, 4.98; Br, 35.19. Found: C, 53.00; H, 5.16; Br, 34.90.

9h: oil; ^{1}H NMR δ 1.05–1.78 (m, 3 H, CH_2 and CH of cyclopropane ring), 2.80–3.27 (m, 1 H, CHBr), 3.82–4.17 (m, 2 H, OCH_2), 6.81–7.28 (m, 4 H, aromatic H); IR (film) 2960–2860, 1580, 1495, 1400, 1280–1240, 1100, 1030, 830, 670, 640 cm^{-1}. Anal. Calcd for $C_{10}H_{10}BrClO$: C, 45.92; H, 3.85. Found: C, 45.75; H, 4.11.

9i: oil; ^{1}H NMR δ 0.74–1.80 (m, 3 H, CH_2 and CH of cyclopropane ring), 2.79–3.25 (m, 1 H, CHBr), 3.75 (s, 3 H, OCH_3), 3.80–4.14 (m, 2 H, OCH_2), 6.81–6.86 (m, 5 H, aromatic H); IR (film) 3000, 2900–2800, 1500, 1455, 1220, 1035, 945, 815 cm^{-1}. Anal. Calcd for $C_{11}H_{13}O_2Br$: C, 51.38; H, 5.43; Br, 31.07. Found: C, 51.68; H, 5.33; Br, 30.95.

9j: oil; bp 105 °C (0.05 mm); ^{1}H NMR δ 0.64–1.50 (m, 3 H, CH_2 and CH of cyclopropane ring), 2.58–3.11 (m, 3 H, SCH_2 and CHBr), 7.19–7.37 (m, 5 H, aromatic H); IR (film) 3070–3050, 3000, 2950–2920, 1590, 1480, 1440, 1310, 1260, 1240, 1095, 1045–1030, 740, 695, 600 cm^{-1}. Anal. Calcd for $C_{10}H_{11}SBr$: C, 49.39; H, 4.56; Br, 32.86; S, 13.19. Found: C, 49.66; H, 4.60; Br, 32.42; S, 13.34.

9k: oil; ^{1}H NMR δ 0.63–1.39 (m, 3 H, CH_2 and CH of cyclopropane ring), 1.50–2.14 (m, 5 H, CH_2 and CH_3), 2.36–2.76 (m, 1 H, CHBr), 7.25–7.50 (m, 5 H, aromatic H); IR (film) 3060–2850, 2240, 1600, 1495, 1445, 1295–1240, 1080–1030, 790–760, 700, 520 cm^{-1}; MS m/e (relative intensity) 266 (M^+ + 2, 3), 265 (M^+ + 1, 4), 264 (M^+, 3), 184 (32), 130 (100), 116 (44), 103 (57), 77 (36), 53 (93), 39 (44). Anal. Calcd for $C_{13}H_{14}BrN$: C, 59.11; H, 5.34; N, 5.30. Found: C, 59.36; H, 5.18; N, 5.34.

9l: oil; bp 178 °C (0.1 mm) (Kugelrohr); ^{1}H NMR δ 0.63–1.27 (m, 3 H, CH_2 and CH of cyclopropane ring), 1.75–2.21 (m, 2 H, CH_2), 2.35–2.83 (m, 1 H, CHBr), 3.08–3.32 (m, 2 H, CH_2Ph), 7.01–7.39 (m, 10 H, aromatic H); IR (film) 3080–3040, 2935, 2850, 2240, 1600, 1590, 1495, 1450, 1260–1245, 1080, 1040, 915, 765, 700 cm^{-1}. Anal. Calcd for $C_{19}H_{18}BrN$: C, 67.07; H, 5.33; Br, 23.48; N, 4.12. Found: C, 67.39; H, 5.59; Br, 23.27; N, 4.27.

8m: mp 37–39 °C (from ethanol); ^{1}H NMR δ 1.16–1.64 (m, 2 H, CH_2 of cyclopropane ring), 2.26–2.44 (m, 1 H, CH of cyclopropane ring), 5.51–5.60 (m, 2 H, C=CH_2), 7.28–7.44 (m, 10 H, aromatic H); IR (KBr) 3060–2930, 2240, 1490, 1410, 900, 760, 740, 700 cm^{-1}; MS m/e (relative intensity) 245 (M^+, 17), 244 (M^+ – 1, 48), 205 (36), 190 (36), 167 (100), 154 (60), 129 (38), 116 (72), 91 (5), 89 (11), 77 (17), 51 (22), 39 (10). Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16. Found: C, 88.24; H, 6.28.

9m: mp 105–107 °C (from hexane–methanol mixture); ^{1}H NMR δ 0.78–1.35 (m, 3 H, CH_2 and CH of cyclopropane ring), 2.36–2.66 (m, 3 H, CH_2 and CHBr), 7.32–7.36 (m, 10 H, aromatic H); IR (KBr) 2965, 2920, 2240, 1490, 1445, 1255, 1090–1010, 800, 760, 750, 700 cm^{-1}; MS m/e (relative intensity) 328 (M^+ + 2, 2), 327 (M^+ + 1, 9), 326 (M^+, 3), 325 (M^+ – 1, 9), 246 (19), 193 (33), 165 (100), 115 (13), 77 (9), 53 (42), 39 (24). Anal. Calcd for $C_{18}H_{16}BrN$: C, 66.27; H, 4.94; Br, 24.49; N, 4.29. Found: C, 65.91; H, 5.08; Br, 24.33; N, 4.24.

The Products 9m,n from the Reactions of 1a with 7m,n in a NaH/DMSO System. NaH (0.144 g, 6 mmol) (mineral oil was washed out with hexane) and the solution of the C–H acid **7m** or **7n** (6 mmol) in DMSO (5 mL) were stirred until the thermal effect ceased. Then, the solution of **1a** (0.85 g, 5 mmol) in DMSO (5 mL) was added, and the reaction was carried out at 56–58 °C for 3–5 h. The mixture was worked up as described above, the product **9m** was isolated by crystallization and **9n** by method I (Table I). For physical and spectral properties of **9m**, see above.

9n: oil; ^{1}H NMR δ 0.64–1.46 (m, 3 H, CH_2 and CH of cyclopropane ring), 1.79–2.29 (m, 2 H, CH_2), 2.50–3.23 (m, 1 H, CHBr), 3.75–4.12 (m, 1 H, CHCN), 7.25–7.36 (m, 5 H, aromatic H); IR (film) 3060–3040, 2965, 2850, 2245, 1600, 1495, 1450, 1255, 1080, 1040, 750, 700 cm^{-1}. Anal. Calcd for $C_{12}H_{12}BrN$: C, 57.62; H,

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4.84; Br, 31.94; N, 5.60. Found: C, 57.41; H, 4.77; Br, 31.85; N, 5.63.

Preparation of 9o from 1a and 7o in Solid K_2CO_3/C_6H_6/TBABr System. Powdered K_2CO_3 (2.5 g, 1.8 mmol), benzene (20 mL), TBABr (0.1 g, 0.31 mmol), dimethyl malonate (**7o**) (0.79 g, 6 mmol), and **1a** (0.85 g, 5 mmol) were stirred and refluxed for 5 h. The mixture was then cooled and filtered, and the solid was washed with benzene. The combined filtrates were concentrated, and the product **9o** was isolated by vacuum distillation (Table I): bp 105 °C (0.1 mm); ^1H NMR δ 0.50–1.43 (m, 3 H, CH_2 and CH of cyclopropane ring), 1.82–2.19 (m, 2 H, CH_2), 2.56–3.15 (m, 1 H, CHBr), 3.43–3.78 (m, 7 H, 2 CH_3 and CHCOO); IR (film) 3000, 2950, 1750–1730, 1440, 1345, 1250, 1150, 1040 cm^{-1}; MS *m/e* (relative intensity) 267 ($M^+ + 2$, 1), 266 ($M^+ + 1$, 10), 265 (M^+, 2), 264 ($M^+ - 1$, 8), 201 (21), 185 (37), 153 (35), 132 (100), 125 (40), 100 (23), 59 (17), 39 (10), 27 (8). Anal. Calcd for $C_9H_{13}BrO_4$: C, 40.78; H, 4.94; Br, 30.14. Found: C, 40.63; H, 4.81; Br, 29.89.

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Registry No. (*E*)-**1a**, 95896-07-4; (*Z*)-**1a**, 95896-06-3; **7a**, 71-36-3; **7b**, 111-27-3; **7c**, 112-30-1; **7d**, 108-93-0; **7e**, 100-51-6; **7f**, 636-72-6; **7g**, 108-95-2; **7h**, 106-48-9; **7i**, 150-76-5; **7j**, 108-98-5; **7k**, 1823-91-2; **7l**, 3333-14-0; **7**, 86-29-3; **7n**, 140-29-4; **7o**, 108-59-8; **8a**, 119819-25-9; **8b**, 119819-26-0; **8c**, 119819-27-1; **8d**, 119819-28-2; **8e**, 119819-29-3; **8f**, 119819-30-6; **8m**, 119819-37-3; (*E*)-**9g**, 119819-31-7; (*Z*)-**9g**, 119819-41-9; (*E*)-**9h**, 119819-32-8; (*Z*)-**9h**, 119819-42-0; (*E*)-**9i**, 119819-33-9; (*Z*)-**9i**, 119819-43-1; (*E*)-**9j**, 119819-34-0; (*Z*)-**9j**, 119819-44-2; (*E*)-**9k**, 119819-35-1; (*Z*)-**9K**, 119819-45-3; (*E*)-**9l**, 119819-36-2; (*Z*)-**9l**, 119819-46-4; (*E*)-**9m**, 119819-38-4; (*Z*)-**9m**, 119819-47-5; (*E*)-**9n**, 119819-39-5; (*Z*)-**9n**, 119819-48-6; (*E*)-**9o**, 119819-40-8; (*Z*)-**9o**, 119819-49-7; TEBACl, 56-37-1.

Enantioselective Preparation of Functionalized Cyclopentanoids via a Common Chiral (π-Allyl)palladium Complex[1]

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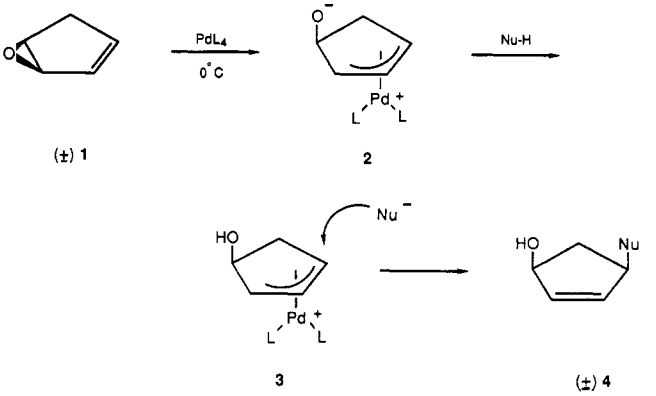
Functionalized cyclopentanoids have provided molecular foundations for the construction of biologically intriguing compounds of diverse medicinal interest.[2,3] The fact that pharmacological response often derives from a single enantiomorph underscores the need for the development of enantiospecific routes to these cyclopentyl backbones. Herein, we report the efficient preparation of potentially useful, optically active cyclopentanoids via a common chiral (π-allyl)palladium complex.

Recently, we[4] and others[5] described a highly direct, palladium-catalyzed route to (±)-*cis*-4-substituted-2-cyclopenten-1-ols (**4**) based on the reaction of mildly acidic nucleophiles with cyclopentadiene monoepoxide (**1**). The mechanism is outlined in Scheme I. The reaction's unusually high stereo- and regiospecificity appears to be governed by the unique structural characteristics of π-allyl complex **3**. The polar hydroxyl functionality maintains regiocontrol by directing the internally generated nucleophile toward the distal end of the π-allyl system[6] while the stereocontrol is regulated by the backside nucleophilic displacement of palladium.[7] Unfortunately, the reaction's usefulness in the preparation of optically active cyclopentanoids is constrained by the unavoidable racemic composition of epoxide **1**.[8] A desire to overcome this limitation coupled with the needs of a related project prompted our search for an optically active alternative to Scheme I.

Scheme I



We were keenly aware that if an enantioselective route to π-allyl **3** could be devised a virtually unlimited number of optically active cyclopentanoids would be potentially accessible from a single resolved source. Therefore, the preparation of enantiomerically pure **3** became the lodestar of our research program.

Several years ago it was discovered that palladium π-allyls could be prepared from allylic acetates and palladium(0) catalysts via a metal-induced ionization of the acetoxy moiety.[9] Subsequent reaction between these transient intermediates and externally generated nucleophiles was found to afford substitution products of predictable stereochemistry yet not always consistent regiochemistry. Since it was known[10] that palladium π-allyls derived from optically active allylic acetates were themselves optically active, we reasoned that exposure of enantiomerically pure allyl acetate **5** to palladium(0) catalyst ought to give rise to a single enantiomorph of (π-allyl)palladium complex **3**. Prompt nucleophile entrapment by this electrophilic species (**3**) was expected to yield substituted cyclopentanoids of homogeneous chirality. Problems associated with regiocontrol were not anticipated during this nucleophilic addition step since complex **3** was expected to deliver the externally generated nucleophiles to the same unhindered terminus of the π-allyl system that it had for the internally generated (Scheme I) counterparts. Thus, provided the starting allyl acetate **5** is enantiomerically enriched and that racemization mechanisms are

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