Table I. Reduction of Selected Organic Compounds with $AlH_3 \cdot NMe_2Et$[a]

compd	temp, °C	[$AlH_3 \cdot NMe_2Et$]/[compd]	time, h	product	$AlH_3 \cdot NMe_2Et$ yield, %	$AlH_3 \cdot THF$ yield, %	ref
caproic acid	0	1.33	3.0	1-hexanol	99[b]	98.5[c]	1
ethyl 3-chloropropionate	0	1.00	0.25	3-chloro-1-propanol	99[d]	100[d]	2
p-nitrobenzoyl chloride	0	1.00	0.5	*p*-nitrobenzyl alcohol	90[e]	92[e]	2
N,N-dimethylbenzamide	25	1.33	0.5	dimethylbenzylamine	98[e]	98[f]	2
benzonitrile	25	1.33	1.0	benzylamine	98[f]	96.8[f]	2

[a] Reactions were in THF–toluene, 0.25 M in compound. Compounds were added to the reagent solution. [b] Yield was determined by ^1H NMR using methylenecyclohexane as an internal standard. [c] Calculated from the number of millimoles of hydride used for reduction reported in the reference. [d] Yields were determined by GC analysis. [e] Isolated yields. [f] Yields were estimated by titration.

Experimental Section

A Perkin-Elmer Plasma II emission spectrometer was used for ICP spectroscopic determination of Al and Li. Active hydride contents were determined by measuring H_2 evolution upon hydrolysis of solutions using a standard gas buret technique.[10] ^1H NMR spectra were recorded on a Varian EM-390 90-MHz NMR spectrometer, and ^{27}Al NMR spectra were recorded on a GE-Nicolet NT 360-MHz NMR spectrometer. The X-ray diffraction pattern was recorded on a Scintag PAD V automated X-ray powder diffractometer.

Preparation of DMEA–Alane. The following procedure for the synthesis of $AlH_3 \cdot NMe_2Et$ in toluene is representative for amine–alane extraction from $LiAlH_4$. All operations were performed under a nitrogen atmosphere. To a slurry of $LiAlH_4$ (7.6 g, 200 mmol) suspended in toluene (200 mL, distilled from $NaAlH_4$) was added dimethylethylamine (50 mL, distilled from $NaAlH_4$ after stirring overnight), and the mixture was magnetically stirred for 16 h. The resulting insoluble solid (3.59 g, corresponding to 66.7 mmol of Li_3AlH_6) was filtered off using a fritted-glass funnel and washed with a small amount of toluene. The combined filtrate (127.9 g) analyzed as 2.77 wt % Al and 0.06 wt % Li by ICP spectroscopy. The total soluble Al (3.54 g, 131.2 mmol) corrected for soluble Li (0.077 g, 10.96 mmol) corresponded to 90% yield of the amine–alane (120.24 mmol). Analysis of the filtered solids by X-ray powder diffraction showed only Li_3AlH_6; no $LiAlH_4$ was detected. An aliquot of the filtrate analyzed as 3.16 mmol of active H per gram of filtrate upon hydrolysis (404.2 mmol total, Al:H = 1.00:3.08). ^1H NMR in C_6D_6: δ 3.94 (s, 3 H, AlH_3), 2.27 (q, 2 H, NCH_2CH_3), 1.96 (s, 6 H, CH_3), 0.76 (t, 3 H, NCH_2CH_3). ^{27}Al NMR in toluene: δ 108.7 (br s). The yields of other amine–alanes were also determined by analysis of total soluble aluminum corrected for the soluble lithium using ICP spectroscopy. The soluble lithium amounted to about 8% of the theoretical yield of amine–alane with dimethylethylamine, to 10–12% with *N*-methylpyrrolidine and trimethylamine, but to 75% with diethylmethylamine and 92% with triethylamine.

Reduction of Organic Compounds with DMEA–Alane. The following procedure for the reduction of ethyl 3-chloropropionate with $AlH_3 \cdot NMe_2Et$ is representative of the selective reduction of the organic compounds examined. All reductions were carried out under a nitrogen atmosphere. The amine–alane solution in toluene (11.4 mL, 0.88 M) was introduced to a 100-mL round-bottomed flask containing THF (20.3 mL) via a hypodermic syringe and the mixture was cooled to 0 °C. The ester, contained in dry THF (8.3 mL of 1.2 M) previously cooled to 0 °C, was added to the reagent solution with stirring at 0 °C. The formation of a white precipitate was observed immediately. After 15 min, the reaction mixture was hydrolyzed with 6 mL of THF–H_2O (1:1) mixture. 1-Octanol (0.640 g, 4.91 mmol) was added as an internal standard. The organic layer was separated, dried ($MgSO_4$), and analyzed by GC using a 60-m FFAP capillary column for 9.91 mmol of 3-chloro-1-propanol (99% yield). The yield of benzylamine was determined by titration, the yields of dimethylbenzylamine and *p*-nitrobenzyl alcohol were determined by isolation, and the yield of 1-hexanol was determined by ^1H NMR with methylenecyclohexane as an internal standard. These products were all confirmed by ^1H NMR.

Acknowledgment. The X-ray powder diffraction spectrum was recorded by Dr. W. D. Pitts, the ^{27}Al NMR spectrum was recorded by P. K. Landry, and ICP spectroscopy was performed by Dr. D. A. Goff of Ethyl Corp.

Registry No. $LiAlH_4$, 16853-85-3; Me_2NEt, 598-56-1; $MeN(CH_2)_4$, 120-94-5; Me_3N, 75-50-3; Et_2NMe, 616-39-7; Et_3N, 121-44-8; $AlH_3 \cdot Me_2EtN$, 124330-23-0; $AlH_3 \cdot MeN(CH_2)_4$, 126084-10-4; $AlH_3 \cdot (Me_3N)_2$, 17211-58-4; $AlH_3 \cdot MeEt_2N$, 123031-51-6; $AlH_3 \cdot Et_3N$, 12076-08-3; $Me(CH_2)_4CO_2H$, 142-62-1; $ClCH_2CH_2CO_2Et$, 623-71-2; *p*-$NO_2C_6H_4COCl$, 122-04-3; $PhCONMe_2$, 611-74-5; PhCN, 100-47-0; $Me(CH_2)_5OH$, 111-27-3; $Cl(CH_2)_3OH$, 627-30-5; *p*-$NO_2C_6H_4CH_2OH$, 619-73-8; $PhCH_2NMe_2$, 103-83-3; $PhCH_2NH_2$, 100-46-9.

Supplementary Material Available: ^1H and ^{27}Al NMR spectra of DMEA–alane and X-ray powder diffraction spectrum of the filtered solids (3 pages). Ordering information is given on any current masthead page.

(10) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975.

Novel Neutral Alkylations of Indoles and Pyrroles with Vinyl Epoxides at High Pressure[1]

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Received October 3, 1989

In organic synthesis, the most important reaction is alkylation. Alkylation reactions are generally catalyzed by either acid or base, but obviously, the mildest way to perform these reactions is to conduct them under neutral conditions. The high-pressure technique as one of these approaches has seen increased use in recent years.[2] As a part of our program to develop new synthetic methods in this field,[3] it has become of interest to investigate the alkylation of indoles or pyrroles. In this paper we describe an essentially noncatalyzed carbon–carbon bond formation of indoles and pyrroles with vinyl epoxides. The procedure constitutes a useful method to produce tryptophol derivatives, which are of interest as synthetic intermediates toward antibiotics such as indolmycin.[4]

Although it is known that indoles react with some epoxides with the assistance of Lewis acid catalysts or

(1) High-Pressure Organic Chemistry. 10. For part 9, see ref 3a.
(2) For reviews of this area, see: (a) *Organic High Pressure Chemistry*; le Noble, W. J., Ed.; Elsevier: Amsterdam, 1988. (b) Matsumoto, K.; Sera, A.; Uchida, T. *Synthesis* **1985**, 1. (c) Matsumoto, K.; Sera, A. *Ibid.* **1985**, 999.
(3) (a) Kotsuki, H.; Ichikawa, Y.; Nishizawa, H. *Chem. Lett.* **1988**, 673. (b) Kotsuki, H.; Mori, Y.; Ohtsuka, T.; Nishizawa, H.; Ochi, M.; Matsuoka, K. *Heterocycles* **1987**, *26*, 2347.
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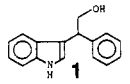
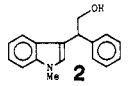
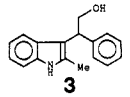
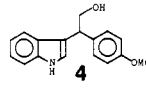
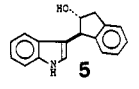
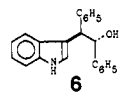
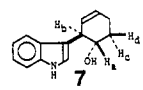
0022-3263/90/1955-2969$02.50/0

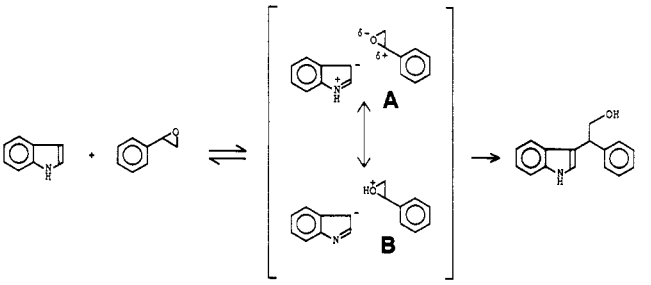
Table I. High-Pressure Reaction of Indoles with Vinyl Epoxides[a]

entry	indole	epoxide	temp, °C	product	yield, %[b]	mp, °C
1			85	 1	13[c]	
2			42		56	120.0-120.5
3			42		66[d]	
4			42	 2	13	oil
5			42	 3	44	oil
6			42	 4	90	117.5-118.5
7			42	 5	58	oil
8			62	 6	12	oil
9			62	 7	38	131.5-132.0

[a] Unless otherwise noted, all reactions were conducted in acetonitrile at 10 kbar for 24 h. Substrate ratio was constantly 1:1. [b] Isolated yields of the pure compounds. The unreacted starting materials were cleanly recovered in each case. [c] At atmospheric pressure. [d] One equivalent of water was added to the system.

Grignard reagents,[5] to explore such a mild synthetic procedure will be valuable because of the labile nature of the indole nucleus. For this purpose, we anticipated that high-pressure chemistry would be advantageous, since it has been reported that such a bimolecular alkylation reaction requires a relatively large molar volume contraction.[6] Thus, when a 1:1 mixture[7] of indole and styrene oxide in acetonitrile was reacted at 10 kbar and 42 °C followed by preparative TLC, a 56% yield of 2-(3-indolyl)-2-phenylethanol (1) was obtained.[8,9] The structure of 1 was confirmed by ^1H and ^{13}C NMR spectra, and an INEPT experiment[10] clarified that a hydroxy group is bonded to the methylene carbon absorbing at 66.49 ppm. In a control experiment for comparison, heating the same mixture at atmospheric pressure and at 85 °C for 24 h gave only 13% yield of product. Furthermore, the use of indolylmagnesium bromide[11] as a strong nucleophile (at room temperature for 2 days) yielded 33% of 1. These facts clearly demonstrated the feasibility of our initial goal.

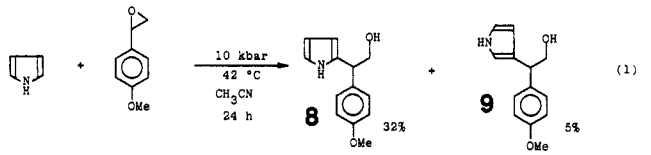
Scheme I

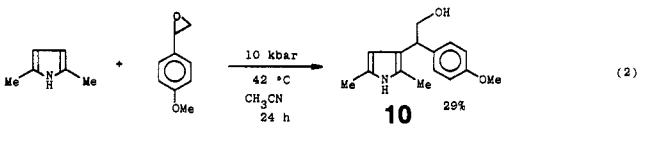


The scope and efficiency of this method are summarized in Table I. From these results a number of characteristic features can be identified. (1) Substitution on the indole nucleus occurred exclusively at the 3-position. In accordance with this finding, 3-methylindole gave no adducts. This result provides a remarkable contrast to the similar reactions under Pd catalysis, where N-alkylation is predominant.[12] (2) Regioselective epoxide ring opening at the benzylic or allylic position implies that the reaction proceeds through the stabilized cationic intermediates. (3) Epoxide-opening stereochemistry occurs cleanly in a trans fashion, consistent with the general mechanism of the epoxide chemistry (entries 7–9).[13] For example, the trans stereochemistry for 7 was assigned from the ^1H NMR spectra (400 MHz) in which H_a (δ 3.96) shows a clear ddd pattern having coupling constants of J_{ab} = 10.1 Hz, J_{ac} = 7.7 Hz, and J_{ad} = 3.2 Hz.

Interestingly, 2-methylindole was a better nucleophile than 1-methylindole (entries 4 and 5). Furthermore, although this has only been briefly studied, the addition of water to this system slightly increased the product yield (entry 3). To account for these results, we propose the mechanism depicted in Scheme I. Under high-pressure conditions indole might behave as a proton donor to facilitate the epoxide-opening reaction. Since 1-acetylindole and other epoxides such as cyclohexene oxide, methyl 2,3-epoxy-3-methylbutyrate,[14] and benzyl 2,3-epoxypropyl ether were found to be nonreactive, it seems likely that the resonance structures A and B play an important role in these reactions. This explanation is again supported by the fact that the ionization process is promoted by applying high pressure.[15]

In order to evaluate the utility of high-pressure reactions, we have further examined the possibility of the alkylation of pyrroles with vinyl epoxides (eqs 1 and 2). Unfortunately, pyrrole itself was less reactive than indole but re-





(5) Houlihan, W. J. *Indoles*; Wiley: New York, 1972; Vol. 1. Sundberg, R. J. *The Chemistry of Indoles*; Academic Press: London, 1970.

(6) It is generally recognized that bond formation shows a large volume contraction: −10 cm³/mol. For comprehensive lists of several organic reactions, see: le Noble, W. J. *Prog. Phys. Org. Chem.* **1967**, *5*, 207. See also: Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407. le Noble, W. J.; Asano, T.; van Eldik, R. *Ibid.* **1989**, *89*, 549.

(7) The use of a 1:2 or 2:1 ratio of the substrates did not improve the product yield.

(8) All yields described here were based on the reacted starting materials. Unreacted substrates were cleanly recovered.

(9) For the description of our high-pressure apparatus, see: Kotsuki, H.; Nishizawa, H.; Kitagawa, S.; Ochi, M.; Yamasaki, N.; Matsuoka, K.; Tokoroyama, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 544.

(10) Derome, A. E. *Modern NMR Techniques for Chemical Research*; Pergamon Press: Oxford, 1987; pp 133–143.

(11) Heath-Brown, B.; Philpott, P. G. *J. Chem. Soc.* **1965**, 7165.

(12) Trost, B. M.; Molander, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5969.

(13) Kirk, D. N. *Chem. Ind. (London)* **1973**, 109. Buchanan, J. G.; Sable, H. Z. In *Selective Organic Transformations*; Thyagarajan, B. S., Ed.; Wiley: New York, 1972; Vol. 2, p 1. Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737.

(14) This result means our novel technique cannot be applied for the preparation of synthetic intermediates required for antibiotics such as indolmycin. See ref 4.

(15) Activation volume for ionization is −20 cm³/mol. See ref 6.

acted with *p*-methoxystyrene oxide to give **8** and **9** in 32 and 5% yields, respectively.[16] Similarly, treatment of 2,5-dimethylpyrrole with *p*-methoxystyrene oxide provided **10** in 29% yield as the sole product. These adducts were quite unstable upon storage even under a nitrogen atmosphere, and hence the preparation under normal conditions will be strictly limited.

Since the starting compounds of vinyl epoxides are readily accessible from dienes by selective monoepoxidation,[17] the results presented above demonstrate the potential utility of high-pressure technology as a convenient route to tryptophol derivatives.

Experimental Section

All melting points are uncorrected. The NMR spectra were recorded on a Hitachi R-90H spectrometer (90 MHz for ^{1}H NMR analysis and 22.6 MHz for ^{13}C NMR analysis) or on a JEOL GX-400 spectrometer (400 MHz for ^{1}H NMR analysis) with TMS as an internal standard. The IR spectra were measured with a JASCO Model A-302 infrared spectrophotometer. High-resolution mass spectra were obtained with a JEOL HX-100 spectrometer. Preparative TLC was carried out on 2-mm-thick Merck Kieselgel 60PF-254.

Acetonitrile was distilled from CaH_2. The following epoxides were freshly prepared according to the literature procedure: indene oxide,[17] 1,3-cyclohexadiene monoepoxide,[17] and *p*-methoxystyrene oxide.[18]

Typical Procedure for the Reaction of Indole with Styrene Oxide. A mixture of indole (117 mg, 1 mmol) and styrene oxide (120 mg, 1 mmol) in acetonitrile (ca. 1 mL) was placed in a Teflon reaction vessel and allowed to react at 10 kbar and 42 °C for 24 h.[9] The crude sample was separated by preparative TLC (hexane/ethyl acetate, 1:1) to give 134 mg (56%) of **1**.

2-(3-Indolyl)-2-phenylethanol (1): IR ($CHCl_3$) 3610, 3510, 1620, 1600, 1500, 1455, 1340, 1100, 1040, 1015, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.59 (1 H, br s), 4.15 (1 H, dd, J = 10.5, 6.7 Hz), 4.23 (1 H, dd, J = 10.5, 6.7 Hz), 4.47 (1 H, t, J = 6.7 Hz), 7.03 (1 H, ddd, J = 8.1, 7.1, 1.0 Hz), 7.07 (1 H, d, J = 2.0 Hz), 7.16 (1 H, ddd, J = 8.1, 7.1, 1.0 Hz), 7.21 (1 H, m), 7.26–7.36 (5 H, m), 7.44 (1 H, dd, J = 8.1, 0.7 Hz), 8.05 (1 H, br s); ^{13}C NMR ($CDCl_3$) δ 45.74, 66.49, 111.18, 116.22, 119.43, 119.62, 121.94, 122.35, 126.76, 127.14, 128.35 (×2), 128.64 (×2), 136.61, 141.76. Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.94; H, 6.40; N, 5.85.

2-(1-Methyl-3-indolyl)-2-phenylethanol (2): IR (neat) 3370, 3050, 3030, 2940, 2870, 1615, 1605, 1485, 1470, 1375, 1330, 1050, 910, 735, 705 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.58 (1 H, br s), 3.75 (3 H, s), 4.1–4.6 (3 H, m), 6.94 (1 H, s), 7.0–7.5 (9 H, m); ^{13}C NMR ($CDCl_3$) δ 32.61, 45.60, 66.39, 109.14, 114.44, 118.89, 119.32, 121.70, 126.49, 126.55, 127.37, 128.16 (×2), 128.41 (×2), 137.10, 141.82; HRMS calcd for $C_{17}H_{17}NO$ 251.1310, found 251.1337.

2-(2-Methyl-3-indolyl)-2-phenylethanol (3): IR (neat) 3400, 3050, 3030, 2920, 2880, 1620, 1600, 1580, 1495, 1460, 1300, 1265, 1050, 1030, 1010, 735, 700 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.63 (1 H, br s), 2.32 (3 H, s), 4.1–4.6 (3 H, m), 6.9–7.5 (9 H, m), 7.86 (1 H, br); ^{13}C NMR ($CDCl_3$) δ 12.00, 44.99, 64.90, 109.87, 110.48, 118.92, 119.23, 120.75, 126.09, 127.55, 127.80 (×2), 128.19 (×2), 133.10, 135.30, 141.64; HRMS calcd for $C_{17}H_{17}NO$ 251.1310, found 251.1286.

2-(3-Indolyl)-2-(4-methoxyphenyl)ethanol (4): IR ($CHCl_3$) 3560, 3460, 1610, 1580, 1510, 1450, 1240, 1175, 1030, 1010, 820 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.65 (1 H, br s), 3.75 (3 H, s), 4.0–4.5 (3 H, m), 6.82 (2 H, d, J = 8.8 Hz), 6.95–7.5 (5 H, m), 7.23 (2 H, d, J = 8.8 Hz), 8.05 (1 H, br); ^{13}C NMR ($CDCl_3$) δ 44.83, 55.26, 66.51, 111.12, 114.01 (×2), 116.30, 119.35, 119.44, 121.73, 122.19, 126.94, 129.17 (×2), 133.62, 136.46, 158.29. Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.31; H, 6.39; N, 5.20.

***trans*-3-Hydroxy-2-(3-indolyl)benzocyclopentane (5)**: IR (neat) 3410, 3300, 2970, 1620, 1610, 1460, 1355, 1340, 1105, 1055, 740 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 2.10 (1 H, br), 2.95 (1 H, dd, J = 15.5, 6.8 Hz), 3.30 (1 H, dd, J = 15.5, 6.6 Hz), 4.43 (1 H, d, J = 6.2 Hz), 4.66 (1 H, dt, J = 6.6, 6.2 Hz), 6.87 (1 H, d, J = 2.0 Hz), 6.9–7.50 (8 H, m), 8.00 (1 H, br); ^{13}C NMR ($CDCl_3$) δ 39.99, 51.60, 80.38, 111.30, 115.81, 119.23, 119.50, 121.97, 122.43, 124.63, 124.99, 126.67, 126.76, 126.94, 136.70, 139.99, 143.32; HRMS calcd for $C_{17}H_{15}NO$ 249.1154, found 249.1131.

For the convenience of ^{1}H NMR analysis, **5** was converted to the corresponding *O*-acetate in the usual manner: IR (neat) 3410, 1730, 1370, 1240, 1040, 1020, 785, 750, 740 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (3 H, s), 2.95 (1 H, dd, J = 16.4, 4.4 Hz), 3.48 (1 H, dd, J = 16.4, 6.4 Hz), 4.73 (1 H, d, J = 4.4 Hz), 5.54 (1 H, dt, J = 6.4, 4.4 Hz), 6.70 (1 H, d, J = 2.0 Hz), 7.10 (1 H, t, J = 7.6 Hz), 7.18–7.31 (5 H, m), 7.35 (1 H, d, J = 8.3 Hz), 7.65 (1 H, d, J = 8.1 Hz), 7.94 (1 H, br).

***trans*-2-(3-Indolyl)-1,2-diphenylethanol (6)**: IR (neat) 3550, 3420, 3060, 3040, 1615, 1600, 1490, 1450, 1335, 1030, 1010, 910, 730, 700 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 2.10 (1 H, br), 4.59 (1 H, d, J = 6.6 Hz), 5.50 (1 H, br d, J = 6.6 Hz), 6.9–7.5 (15 H, m), 7.93 (1 H, br); ^{13}C NMR ($CDCl_3$) δ 51.02, 76.63, 110.90, 116.85, 119.17, 119.32, 121.97, 122.49, 126.58 (×2), 126.73, 126.97, 127.31, 127.95 (×2), 128.25 (×2), 129.32 (×2), 135.97, 140.17, 142.77; HRMS calcd for $C_{22}H_{19}NO$ 313.1467, found 313.1494.

***trans*-2-(3-Indolyl)-3-cyclohexen-1-ol (7)**: IR ($CHCl_3$) 3570, 3480, 2990, 2920, 1615, 1450, 1410, 1350, 1335, 1090, 1050 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (1 H, ddt, J = 12.7, 10.7, 7.7 Hz), 1.94 (1 H, br s), 2.04 (1 H, ddt, J = 12.7, 5.1, 3.2 Hz), 2.28 (2 H, m), 3.54 (1 H, ddd, J = 10.1, 4.5, 3.2 Hz), 3.96 (1 H, ddd, J = 10.1, 7.7, 3.2 Hz), 5.70 (1 H, ddd, J = 9.9, 4.5, 1.9 Hz), 5.81 (1 H, ddd, J = 9.9, 6.2, 3.2 Hz), 6.95 (1 H, d, J = 2.2 Hz), 7.08 (1 H, t, J = 7.1 Hz), 7.17 (1 H, dd, J = 8.1, 7.1 Hz), 7.29 (1 H, d, J = 7.1 Hz), 7.65 (1 H, d, J = 8.1 Hz), 8.12 (1 H, br s); ^{13}C NMR ($CDCl_3$) δ 24.47, 29.19, 43.06, 71.94, 111.27, 116.85, 119.35, 119.53, 122.12, 122.46, 126.67, 126.85, 128.62, 136.73. Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.80; H, 7.10; N, 6.49.

2-(2-Pyrrolyl)-2-(4-methoxyphenyl)ethanol (8): IR (neat) 3350, 1610, 1510, 1240, 1175, 1030, 720 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.76 (1 H, br), 3.74 (3 H, s), 3.85–4.25 (3 H, m), 5.96 (1 H, m), 6.14 (1 H, dd, J = 6.0, 3.0 Hz), 6.66 (1 H, m), 6.81 (2 H, d, J = 8.8 Hz), 7.10 (2 H, d, J = 8.8 Hz), 8.30 (1 H, br); ^{13}C NMR ($CDCl_3$) δ 46.27, 55.32, 66.63, 105.63, 108.16, 114.20 (×2), 117.09, 129.26 (×2), 132.19, 132.34, 158.65; HRMS calcd for $C_{13}H_{15}NO_2$ 217.1103, found 217.1080.

2-(3-Pyrrolyl)-2-(4-methoxyphenyl)ethanol (9): IR (neat) 3380, 1610, 1510, 1240, 1175, 1050, 1025, 770, 730 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.65 (1 H, br s), 3.74 (3 H, s), 3.97 (3 H, m), 6.07 (1 H, dd, J = 3.7, 2.5 Hz), 6.56 (1 H, m), 6.70 (1 H, t, J = 2.5 Hz), 6.80 (2 H, d, J = 8.8 Hz), 7.18 (2 H, d, J = 8.8 Hz), 8.18 (1 H, br); ^{13}C NMR ($CDCl_3$) δ 46.11, 55.29, 67.18, 107.89, 113.95 (×2), 115.75, 118.28, 123.89, 129.11 (×2), 134.63, 158.19; HRMS calcd for $C_{13}H_{15}NO_2$ 217.1103, found 217.1076.

2-(2,5-Dimethyl-3-pyrrolyl)-2-(4-methoxyphenyl)ethanol (10): IR (neat) 3340, 2900, 1600, 1575, 1505, 1235, 1170, 1045, 1025, 815, 770 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.88 (1 H, br), 2.06 (3 H, s), 2.16 (3 H, s), 3.73 (3 H, s), 3.91 (3 H, br s), 5.73 (1 H, br d, J = 2.2 Hz), 6.79 (2 H, d, J = 8.8 Hz), 7.17 (2 H, d, J = 8.8 Hz), 7.68 (1 H, br); ^{13}C NMR ($CDCl_3$) δ 11.05, 12.97, 44.68, 55.11, 66.79, 104.41, 113.77 (×2), 118.13, 123.04, 125.39, 128.74 (×2), 134.93, 157.83; HRMS calcd for $C_{15}H_{19}NO_2$ 245.1416, found 245.1400.

Acknowledgment. We thank Dr. Ayumi Ohsaki of Kinki University for measurements of the high-resolution mass spectra and also Dr. Kazuhiko Asao of Osaka City University for the 400-MHz NMR spectra.

Registry No. 1, 57642-28-1; 2, 125879-68-7; 3, 125879-69-8; 4, 125879-70-1; 5, 125879-71-2; 5 (*o*-acetate), 125879-77-8; 6, 125879-72-3; 7, 125879-73-4; 8, 125879-74-5; 9, 125879-75-6; 10,

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125879-76-7; indole, 120-72-9; 1-methylindole, 603-76-9; 2-methylindole, 95-25-5; pyrrole, 109-97-7; 2,5-dimethylpyrrole, 625-84-3; phenyloxirane, 96-09-3; 4-methoxyphenyloxirane, 6388-72-3; 1a*H*-6,6a-dihydroindeno[1,2-*b*]oxirane, 768-22-9; *trans*-diphenyloxirane, 1439-07-2; 7-oxabicyclo-2-heptene, 6705-51-7.

Improved Synthesis of Dimethylketene Trimethylsilyl Acetals by Rhodium-Catalyzed Hydrosilylation

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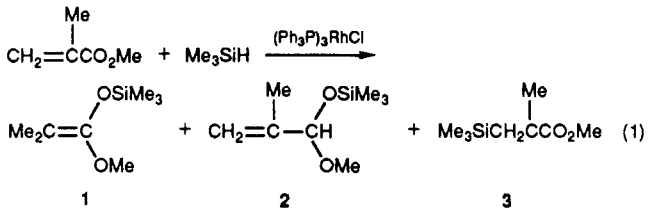
Received April 26, 1988

Silyl ketene acetals have received much attention in the literature since the early work of McElvain and co-workers.[1,2] These ester enolate equivalents are used extensively in Michael additions[3] and aldol condensations.[4] Webster and co-workers have used silyl ketene acetals in an acrylate polymerization technique known as group-transfer polymerization (GTP).[5] In GTP, a silyl ketene acetal initiates condensation polymerization of acrylates and continues through sequential Michael additions.

One route to silyl ketene acetals involves the reaction of an alkali-metal enolate with a chlorosilane.[6] Transition-metal-catalyzed hydrosilylations of α,β-unsaturated esters have also been used.[7-9] While the use of platinum catalyst has been reported,[9] rhodium catalysts are more frequently used.[8] The disadvantage of the rhdoium catalysis method is the formation of inseparable isomers, which reduce the purity of the isolated product. Ojima and co-workers,[8] for example, reported the $(Ph_3P)_3RhCl$-catalyzed preparation (sealed ampule) of several dimethylketene silyl acetals in GC yields of 80–96%. The silyl acetals were not isolated as pure compounds but contained 5–25% of a 1,2-carbonyl adduct. Nevertheless, the overall benefits of a catalytic procedure led us to reinvestigate the rhodium catalysis route.

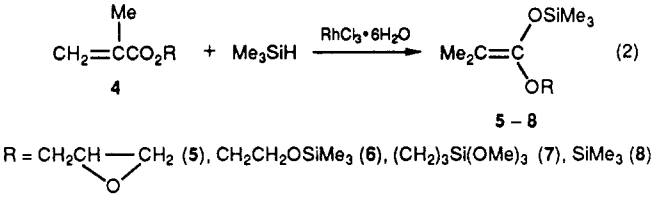
A solution of methyl methacrylate (MMA), 16% molar excess of trimethylsilane, and 400 molar ppm $(Ph_3P)_3RhCl$ was stirred under nitrogen in a Parr pressure reactor for 5 h at 100 °C. Gas chromatographic–mass spectral (GC–MS) examination of the product mixture showed 1-methoxy-1-(trimethylsiloxy)-2-methylprop-1-ene (**1**),[10] as the major product, the 1,2-carbonyl adduct **2**,[11] and the vinyl addition product **3**[12] (eq 1). The GC (with FID) area ratio



was 7:1:1, respectively, with an isolated yield of 50–60% for **1** and a substantial amount of poly(MMA). Lowering the temperature favored less polymer formation, with only a slight increase in the **1**:**2** ratio. Silyl ketene acetal **1** could not be isolated from **2** by distillation.

The total amount of trimethylsilane used and its rate of consumption up to the stoichiometric end point had a significant effect on the product distribution. For example, a reaction of MMA with a stoichiometric amount of trimethylsilane and a reaction with 30% molar excess of trimethylsilane were each carried out. Only the reaction with 30% excess showed a loss of adduct **2** after 5 h at 50 °C. Treatment of an isolated mixture of **1**, **2**, and **3** with excess trimethylsilane and $(Ph_3P)_3RhCl$ results in a decrease in **2**, without change in **1** or **3**. On the other hand, a slower addition rate of the silane afforded an 80% yield of **1** and a 0.3% yield of **3**. The rate of trimethylsilane consumption was faster with $RhCl_3{\cdot}6H_2O$, and conversion to product was almost instantaneous at 50 °C. Thus, the reaction could be carried out at a faster addition rate, and it could be done in a standard round-bottom flask, instead of a sealed ampule or pressure reactor. A modest increase in the yield of **1** to 85% was also obtained with $RhCl_3{\cdot}6H_2O$, and the product did not contain **2** or **3** after distillation (>98% pure).

The verstaility of this improved procedure was demonstrated when excess trimethylsilane and $RhCl_3{\cdot}6H_2O$ were used to prepare the dimethylketene trimethylsilyl acetals shown in eq 2. Furthermore, synthesis of a difunctional silyl ketene acetal **9** was achieved in 75% isolated yield from ethylene glycol dimethylacrylate (see Experimental Section). The amount of polymer formed was ~1% when 2,6-di-*tert*-butyl-4-methylphenol was added, and the reaction was conducted under nitrogen containing 2% oxygen.



Experimental Section

Reagents and chemicals were used as received from the manufacturers unless otherwise specified. Trimethylsilane, trimethylsilyl methacrylate, 3-(trimethylsiloxy)ethyl methacrylate, and 3-(trimethoxysilyl)propyl methacrylate were obtained from

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(11) The spectral data were similar to those reported elsewhere for analogous compounds: GC–MS *m/e* (% rel int) 159 (22, P – 15), 143 (24), 133 (94), 89 (69), 73 (100); GC FT-IR 1060 cm^{-1} for SiOC; NMR ($DCCl_3$) 1.7 (s, 3 H), 3.2 (s, 3 H), 3.6 (s, 1 H), 5.0 (m, 2 H) as a mixture containing 1. See ref 8.
(12) The spectra of **3** matched that of an independently synthesized sample. See: Chalk, A. *J. Organomet. Chem.* **1970**, *21*, 207. Speier, J. L.; Webster, J. A.; Barnes, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 974.

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