(−)-Ketone 1 from (−)-Alcohol 6. A solution of 160 mg of optically pure (−)-alcohol **6** in 2 mL of benzene was added to a mixture of 2 drops of CH_3COOH, 4 drops of H_2SO_4, 30 mg of $Na_2Cr_2O_7$, and 0.5 mL of water. The mixture was stirred for 1 h at room temperature and then washed ($NaHCO_3$ and water). The organic layer was dried (Na_2SO_4) and evaporated. A recrystallization in hexane gave 140 mg (87%) of optically pure (−)-ketone **1**: mp 266–267 °C; $[\alpha]^{25}_D$ −270° (*c* 0.104, cyclohexane), $[\alpha]^{25}_D$ −244° (*c* 0.39, benzene); CD λ_{max} ($\Delta\epsilon_{max}$) 300.5 (−5.33), 311.5 (−7.91), 323 (−8.17), 336 nm (−4.37) (*c* 3.02 mmol/L, cyclohexane); UV (cyclohexane) λ_{max} (ϵ_{max}) 301 (37.2), 312 (45.8), 323 (41.0), 335 nm (20.6).

(+)-Ketone 8 from (+)-Ketone 1. The (+)-ketone **1** (53% e.e.) was prepared from (+)-carbonate **7** (53% e.e.) according to the method previously described. A catalytic hydrogenation of ketone **1**[15] on Pd/C gave the saturated ketone **8** (53% e.e.): mp 281–282 °C, $[\alpha]^{25}_D$ +132° (*c* 0.17, cyclohexane) which gives $[\alpha]^{25}_D$ max calcd +250°; CD (corrected for 100% e.e.) λ_{max} ($\Delta\epsilon_{max}$) 301 (4.14), 311.5 (6.13), 324 (6.39), 336.5 (3.37); UV (cyclohexane) λ_{max} (ϵ_{max}) 302 (40.8), 312 (49), 324 (44.2), 337 (24.3) nm.

Acknowledgment. We thank CNRS for financial support.

Registry No.—(±)-**1**, 63864-540-; 1 isomer 1, 63864-55-1; 1 isomer 2, 54383-73-2; (±)-**6**, 63864-56-2; (−)-**6**, 63864-57-3; **7** isomer 1, 63784-77-0; **7** isomer 2, 63814-62-0; (+)-**8**, 63864-58-4; **9a**, 63784-78-1; **9b**, 63784-79-2; (−)-menthyl chloroformate, 14602-86-9.

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An Alternative Synthesis of (±)-α- and (±)-γ-Lycoranes

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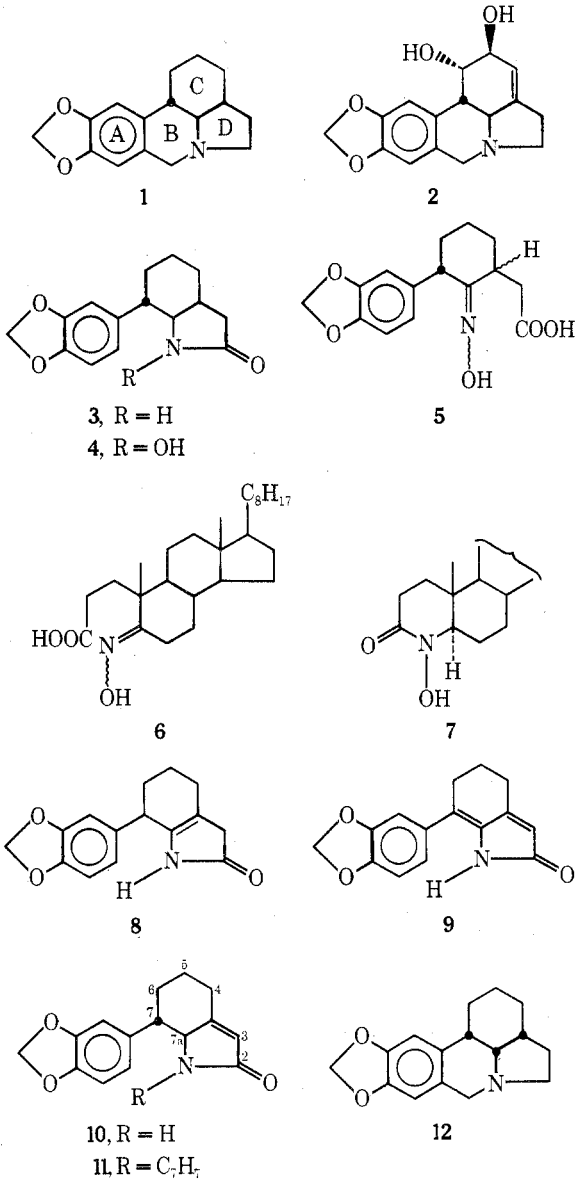
Although an important stereochemical requirement to build up the skeleton of α-lycorane (**1**)[1,2] and lycorine (**2**)[3,4] centers around the construction of the C ring and is successfully fulfilled by application[2,3] of the Diels–Alder reaction, we have searched for another route starting from a cyclohexanone to prepare a lactam (**3**),[2a] which is already converted into **1**. Thus, a cyclic hydroxamic acid (**4**) is considered as an equivalent synthon for **3** and reaction of an oxime (**5**) with zinc dust in boiling acetic acid was carried out in view of the fact[5] that the similar reaction of an oxime (**6**) gives a cyclic hydroxamic acid (**7**) of a six-membered ring. However, we found that reaction of the oxime (**5**) gave unsaturated lactams instead of **4**. Here, we wish to report on the structures of unsaturated lactams **8**, **9**, and **10** and on an alternative synthesis of (±)-α-lycorane (**1**) via unsaturated lactams **10** and **11** and (±)-γ-lycorane (**12**)[2b,c,6] via **9**.



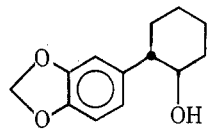
Grignard reaction of cyclohexanone with 3,4-methylenedioxyphenylmagnesium bromide[7] in tetrahydrofuran followed by dehydration and hydroboration oxidation produced a cyclohexanol (**13**) whose Jones oxidation gave a cyclohexanone (**14**).[8] Alkylation of **14** via an enamine and successive alkaline hydrolysis furnished a 2-oxocyclohexylacetic acid (**15**).

Refluxing with zinc dust in glacial acetic acid of the oxime **5** afforded a mixture of lactams A, B, and C. Mass spectra of the lactams A and C showed the same molecular peak at *m/e* 257, which was two mass units less than that of **3**, while that of the lactam B was at *m/e* 255.

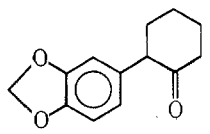
From the spectral data (NMR, IR, and MS), structures of the lactams A, B, and C proved to be **8**, **9**, and **10**, respectively.

It was notable that unsaturated lactams instead of the cyclic hydoxamic acid (4) were obtained in the reaction.

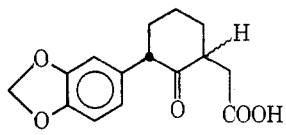
Although two stereoisomers (10 and 16) were possible for the lactam C, the former was favored by the NMR spectrum, which showed a doublet peak (1 H, J = 10 Hz) at δ 3.81 for C-7a hydrogen. Namely, referring to a modified Karplus equation,[9] the observed value of J indicated that the dispositions of C-7 and C-7a hydrogens were trans diaxial.[10] Accordingly, the stereoisomer (16) was ruled out.



13



14



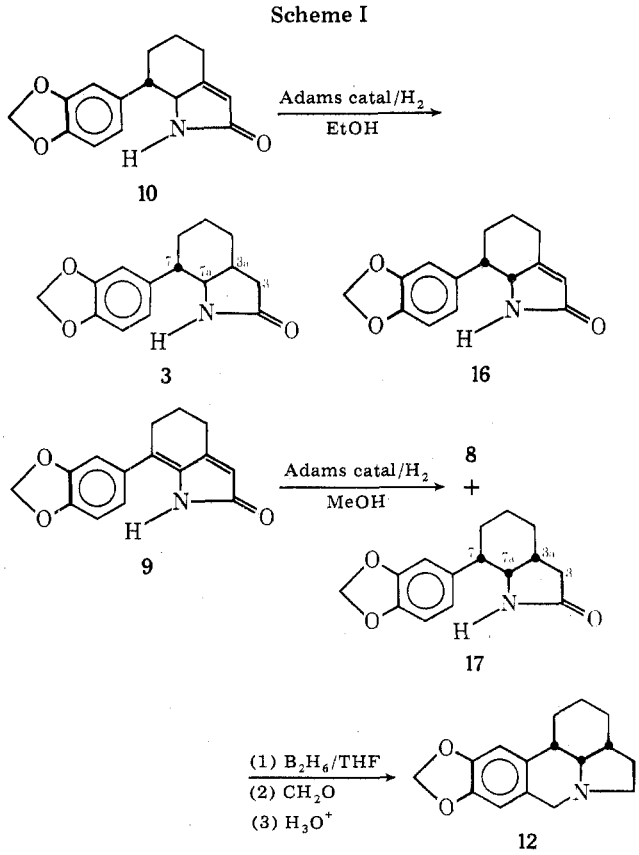
15

Catalytic hydrogenation of 10 gave the lactam 3[2a] whose NMR spectrum exhibited double doublet peaks (1 H, J = 7 and 10 Hz) at δ 3.41 for C-7a hydrogen. Since the lactam is already converted into (±)-α-lycorane (1),[2a] formation of the former constituted the formal synthesis of the latter.

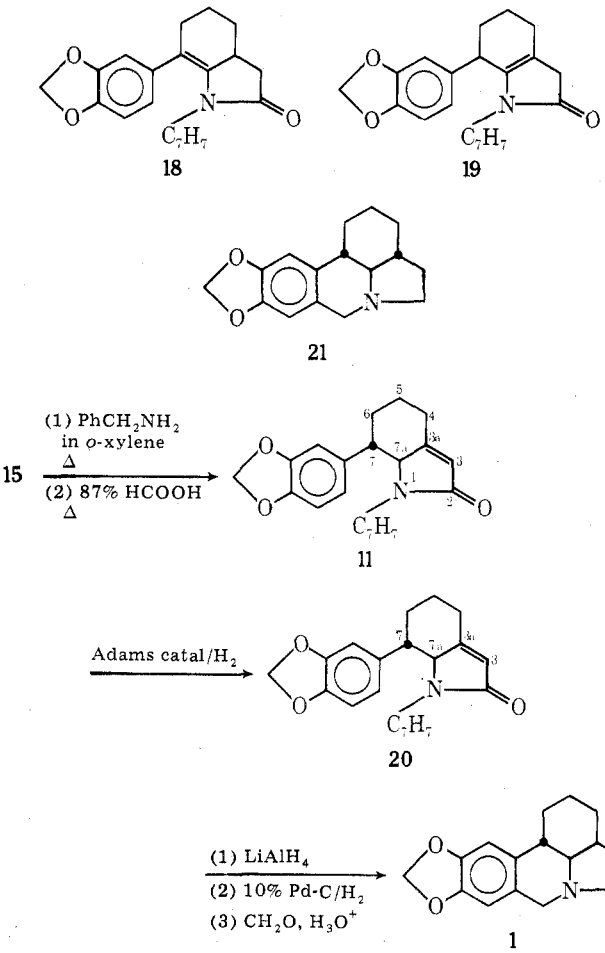
In sharp contrast, the similar reaction of 9 led to a new lactam 17, whose NMR spectrum indicated a triplet peak (1 H, J = 4 Hz) at δ 3.88 for C-7a hydrogen, besides the lactam 8. Reduction of 17 followed by the Pictet–Spengler reaction gave (±)-γ-lycorane (12). The finding[11] revealed that three substituents of the C ring in 17 were all cis oriented.

Formation of 10 in the reaction suggested that if an unsaturated lactam such as 18[12] or 19 could be produced its acid treatment would lead to a lactam 11 predominantly by isomerization of the double bond to the α,β-unsaturated system. Thus, refluxing of 15 with benzylamine in o-xylene

Scheme I



Scheme II



followed by 87% formic acid yielded an amorphous unsaturated lactam 11 whose mass spectrum showed a molecular peak at m/e 347 ($C_{22}H_{21}NO_2$) and a base peak at m/e 91 ($C_7H_7^+$). IR and NMR spectra of 11 exhibited an absorption band at 1680 cm^{-1} for a lactam carbonyl, a doublet peak (1 H, J = 10 Hz) at δ 3.78 for C-7a hydrogen, and a singlet (1 H) at δ 5.91 for C-3 hydrogen, respectively. It was supported by the NMR spectrum that stereochemistry of 11 was the same as that of 10.

Catalytic hydrogenation of 11 afforded a saturated lactam 20 as a sole product. The NMR spectrum of 20 showed diffuse double doublet peaks[14] (1 H, J = 6.25 and 10 Hz) at δ 3.37 for C-7a hydrogen, suggesting that stereochemical features of 20 were similar to those of the lactam 3. Furthermore, the suggestion was substantiated by the result that 20 was not converted into β-lycorane (21)[1c,2a,d] but α-lycorane (1).

As expected, reduction of 20 followed by debenzylation and the Pictet–Spengler reaction gave exclusively (±)-α-lycorane (1) in a moderate yield.

Experimental Section[15]

***trans*-2-(3',4'-Methylenedioxyphenyl)cyclohexanol (13).** To an ice-cooled, stirred solution of Grignard reagent[7] in anhydrous THF [prepared from 5-bromobenzo-1,3-dioxole[16] (45 g), magnesium turnings (6.6 g), and iodine (catalytic amount) in anhydrous THF (200 mL)] was added dropwise at 0–5 °C a solution of cyclohexanone (22.5 g) in anhydrous THF (40 mL) under nitrogen over a period of 1 h. To the stirred solution was added at 0 °C 10% HCl (100 mL) and the whole was heated at 50–60 °C with stirring for 1 h. After cooling, the organic layer was separated and the aqueous solution was extracted with ether. The combined organic layer was washed with brine and dried ($MgSO_4$). Removal of the solvent gave 43.4 g of an oil, which was distilled fractionally furnishing 40.1 g (88.7%) of a pale yellow oil, bp 120–160 °C (40 mm). To a stirred mixture of the oil (20.5 g) and $NaBH_4$ (3.53 g) in anhydrous THF (100 mL) was added dropwise at 20–25 °C a solution of BF_3-etherate (17 g) in anhydrous THF (50 mL)

under nitrogen over a period of 45 min. Excess of the hydride was decomposed under ice cooling with H_2O (50 mL) and 10% NaOH (153 mL). To the stirred mixture was added dropwise at 20–25 °C 30% H_2O_2 (92 mL) over a period of 45 min. After 1 h of agitation, the same workup as noted above gave 20.1 g of a pale yellow oil, which was distilled to afford 17.5 g (82.5%) of a colorless viscous oil (**13**), bp 150–175 °C (4 mm). The oil was triturated in *n*-hexane to lead to a solid, which was recrystallized from *n*-hexane–petroleum ether furnishing 16.8 g (75%) of colorless prisms: mp 63 °C; IR ($CHCl_3$) 3580 (OH) cm^{-1}; NMR δ 3.60 (m, 1, C(1)H), 5.95 (s, 2, OCH_2O), 6.67–6.87 (m, 3, aromatic H). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.49; H, 7.35.

2-(3′,4′-Methylenedioxyphenyl)cyclohexanone (14). Jones reagent[17] (114 mL) was added dropwise to an ice-cooled, stirred solution of **13** (51.3 g) in acetone (1200 mL) over a period of 1.5 h and stirring was continued at room temperature for 1 h. The condensed mixture at reduced pressure (below 30 °C) was poured into ice-cooled brine (1000 mL) and the product was taken up in ether. The ether extract was washed with 5% aqueous $NaHCO_3$ and brine and dried ($MgSO_4$). Evaporation of the solvent gave 45.2 g of a brown oil, which was extracted with hot *n*-hexane. Condensation of the solvent gave 23 g of pale yellow needles, mp 93–94 °C. Distillation of the residue obtained from the mother liquor gave 10.5 g of a pale yellow oil, bp 160–190 °C (4 mm), which was crystallized from acetone–*n*-hexane to afford 9.1 g of pale yellow needles, mp 92–93 °C. Total yield of **14** was 32.1 g (62.6%). Recrystallization from the same solvent furnished colorless needles: mp 92.5 °C (lit.[8] mp 93–94 °C); IR ($CHCl_3$) 1708 (C=O) cm^{-1}; NMR δ 3.50 (m, 1, C(2)H), 5.93 (s, 2, OCH_2O), 6.52–6.82 (m, 3, aromatic H).

3-(3′,4′-Methylenedioxyphenyl)-2-oxocyclohexylacetic Acid (15). An enamine was prepared in the usual manner refluxing **14** (5.45 g) and pyrrolidine (4 g) in anhydrous benzene (150 mL) for 16 h and used after complete evaporation of the solvent at reduced pressure. To a stirred solution of the above enamine in freshly distilled dioxane–benzene (1:1) (100 mL) was added a solution of $BrCH_2COOCH_3$ (7.65 g) in the same solvent (100 mL) during 2 h and refluxing was continued for 15 h. H_2O (50 mL) was added to the mixture and the whole was refluxed for 1 h. To the residue obtained on removal of the solvent at reduced pressure was added CH_3OH (20 mL) and 10% aqueous KOH (20 mL) and the mixture was refluxed for 2 h. The mixture was condensed at reduced pressure, diluted with H_2O, and washed with ether. The usual workup of the ether extract gave 2.4 g of unchanged **14**, mp 80–85 °C. The alkaline solution was acidified with concentrated HCl and the product was taken up in $CHCl_3$. The usual workup of the $CHCl_3$ extract gave 4 g of a solid, which was recrystallized from benzene–*n*-hexane to give 3.1 g (80.7%) of colorless prisms (**15**): mp 124–128 °C; an analytical sample had mp 129–130 °C; IR ($CHCl_3$) 1710 (C=O,COOH) cm^{-1}; NMR δ 2.75 (d, J = 7.5 Hz, 2, $CHCH_2COOH$), 3.60 (m, 1, C(3)H), 5.95 (s, 2, OCH_2O), 6.65–6.90 (m, 3, aromatic H). Anal. Calcd for $C_{15}H_{16}O_5$: C, 65.21; H, 5.84. Found: C, 64.96; H, 5.82.

Oxime 5 of 15. A mixture of **15** (2.1 g) and $NH_2OH{\cdot}HCl$ (2.9 g) in 2 N NaOH (100 mL) was refluxed for 3 h. The mixture was adjusted to pH 2–3 under ice cooling by careful addition of concentrated HCl over a period of 30 min. A resulting precipitate was collected by filtration, washed with cold H_2O, and dried. Recrystallization from aqueous CH_3OH gave 1.66 g (75.4%) of light brown prisms (**5**): mp 137 °C dec; an analytical sample had mp 139–142 °C dec; IR (KBr) 3320 (OH), 1713 (COOH), 1668 (C=N) cm^{-1}. Anal. Calcd for $C_{15}H_{17}NO_5$: C, 61.85; H, 5.88; N, 4.81. Found: C, 61.67; H, 5.85; N, 4.89.

Treatment of 5 with Zinc Dust in Acetic Acid. A mixture of **5** (1.02 g) and zinc dust (1 g) in glacial AcOH (40 mL) was stirred at reflux for 3 h. After cooling, the mixture was filtered and the filtrate was condensed at reduced pressure leading to an amorphous mass, which was dissolved in $CHCl_3$. The $CHCl_3$ solution was washed with 5% aqueous $NaHCO_3$ and brine and dried ($MgSO_4$). Evaporation of the solvent gave 450 mg of an amorphous mass, which was chromatographed over silica gel (10 g). Elution with benzene–$CHCl_3$ (4:1) led to 70.5 mg (7.8%) of **8**, mp 162–165 °C, which was recrystallized from benzene–*n*-hexane yielding colorless prisms: mp 168–171.5 °C; IR (KBr) 3210 (NH), 1670 (CONH) cm^{-1}; NMR δ 2.68–3.10 (m, 1, C(7)H), 5.88 (s, 2, OCH_2O), 6.55–6.88 (m, 3, aromatic H); MS m/e 257 (M^+). Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 69.88; H, 5.72; N, 5.67.

Elution with benzene–$CHCl_3$ (4:2) afforded 138 mg (15%) of **9**, mp 187–189 °C, which was recrystallized from benzene–*n*-hexane producing pale yellow needles: mp 191–192 °C; IR (KBr) 3190 (NH), 1667 (CONH) cm^{-1}; NMR δ 1.92 (quintet, J = 6.3 Hz, 1, C(5)H), 2.57 (t, J = 6.3 Hz, 2, C(6)H), 2.65 (t, J = 6.3 Hz, 2, C(4)H), 5.74 (brs, 1, C(3)H), 5.92 (s, 2, OCH_2O), 6.80 (s, 3, aromatic H); MS m/e 255 (M^+). Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.73; H, 5.20; N, 5.59.

Elution with benzene–$CHCl_3$ (1:1) and $CHCl_3$ furnished 94 mg (10.5%) of **10**, mp 192–197 °C, whose recrystallization from CH_3OH yielded colorless prisms: mp 193–198 °C; IR (KBr) 3170 (NH), 1668 (CONH) cm^{-1}; NMR δ 3.81 (d, J = 10 Hz, C(7a)H), 5.67 (m, 1, NH), 5.73 (brs, 1, C(3)H), 5.90 (s, 2, OCH_2O), 6.60–6.78 (m, 3, aromatic H); MS m/e 257 (M^+). Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 70.14; H, 5.75; N, 5.54.

The alkaline solution was acidified with concentrated HCl and the product was taken up in $CHCl_3$. Usual workup of the $CHCl_3$ extract gave 500 mg of **15**, which was characterized by the IR spectrum.

Catalytic Hydrogenation of 9 and 10. (1) A mixture of **9** (90.2 mg) and Adams catalyst (70 mg) in CH_3OH (18 mL) was shaken at room temperature in hydrogen atmosphere. After filtration of the catalyst, the solvent was removed at reduced pressure to give 89 mg of a solid, which was subjected to preparative TLC[18] over a silica gel GF_{254} plate affording 6.6 mg (7.3%) of **8** (from the faster moving band), whose IR spectrum was identical with that of a sample obtained above, and 76.6 mg (84.8%) of **17** (from the slower moving band). Recrystallization of the latter from benzene–*n*-hexane led to 41.8 mg (46%) of colorless prisms: mp 193–195.5 °C; an analytical sample had mp 194–196 °C; IR ($CHCl_3$) 3420 (NH), 1692 (CONH) cm^{-1}; NMR δ 2.80 (m, 1, C(7)H), 3.88 (t, J = 4 Hz, 1, C(7a)H), 5.04 (brs, 1, NH), 5.96 (s, 2, OCH_2O), 6.62–6.83 (m, 3, aromatic H). Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.43; H, 6.74; N, 5.17.

A mixture melting point of this and Hill's lactam[2a] (mp 191–192 °C) showed appearant depression (mp 160–180 °C).

(2) A mixture of **10** (26.6 mg) and Adams catalyst (13 mg) in CH_3OH (5 mL) was treated in the same manner as noted above to give 27 mg (quantitative yield) of **3**, whose recrystallization from ether furnished colorless needles: mp 191.5–192.5 °C; NMR δ 3.41 (dd, J = 7 and 10 Hz, 1, C(7a)H), 5.88 (brs, 1, NH), 5.96 (s, 2, OCH_2O), 6.60–6.90 (m, 3, aromatic H). This was identical in all respects with Hill's lactam.[2a]

(±)-γ-Lycorane (12). To an ice-cooled solution of **17** (39.4 mg) in anhydrous THF (6 mL) was added 0.92 M diborane–THF (1.5 mL) and the mixture was refluxed for 2.5 h. Excess of diborane was decomposed with 6 N HCl (0.75 mL). The solvent was removed at reduced pressure and the residue was dissolved in H_2O. The mixture was washed with ether and basified with K_2CO_3 (powder). The product was taken up in ether and the usual workup afforded a pale yellow oil (37.2 mg). A mixture of the amine (37.2 mg) and 37% formaline (1.2 mL) in CH_3OH (1.2 mL) was stirred at room temperature for 10 min. To the stirred mixture were added CH_3OH (0.3 mL) and 6 N HCl (3.7 mL) and stirring was continued at room temperature for 3 h. The same workup as noted above gave a pale yellow oil (37.6 mg), which was chromatographed over alumina (Merck Co., Ltd.) to yield 22.1 mg (56.6%) of (±)-γ-lycorane (**12**), mp 66–77 °C. Recrystallization from petroleum ether led to 5.8 mg (14.8%) of colorless prisms, mp 105–106 °C, which were identical in all respects with an authentic specimen.[6a]

(±)-1-Benzyl-*trans*-7,7a*H*-4,5,6,7,7a-pentahydro-7-(3′,4′-methylenedioxyphenyl)-3,3a-dehydroindolin-2-one (11). A mixture of **15** (2.76 g) and benzylamine (1.57 g) in *o*-xylene (60 mL) was refluxed in a flask equipped with a Dean–Stark apparatus for 8 h. The solvent was removed at reduced pressure and the residue was refluxed with 87% HCOOH (20 mL) for 1 h. Evaporation of the solvent at reduced pressure gave a brown oil, which was dissolved in $CHCl_3$. Usual workup of the $CHCl_3$ solution afforded a brown amorphous mass (4.08 g), which was subjected to column chromatography over silica gel (120 g). Elution with benzene–$CHCl_3$ (1:1) and $CHCl_3$ furnished 2.35 g (67.8%) of a pale yellow amorphous product (**11**). All attempts to crystallize failed: IR[19] (film) 1680 cm^{-1} (CON=); NMR δ 3.32 (d, J = 15 Hz, 1, NCHHAr), 3.78 (d, J = 10 Hz, 1, C(7a)H), 4.93 (d, J = 15 Hz, 1, NCHHAr), 5.91 (s, 1, C(3)H), 5.97 (s, 2, OCH_2O), 6.54–6.81 (m, 5, aromatic H), 7.10–7.23 (m, 3, aromatic H); MS m/e 347 (M^+), 91 (base peak).

(±)-1-Benzyl-*trans*-7,7a*H*-*cis*-3,3a*H*-3a,4,5,6,7,7a-hexahydro-7-(3′,4′-methylenedioxyphenyl)indolin-2-one (20). A mixture of **11** (500 mg) and Adams catalyst (50 mg) in C_2H_5OH (50 mL) was shaken at room temperature with hydrogen until uptake of hydrogen ceased. Usual workup of the mixture gave 443 mg (88.6%) of a solid (**20**), mp 132–136 °C, which was recrystallized from *n*-hexane to produce 400 mg (80%) of colorless prisms: mp 137–138 °C; IR (KBr) 1672 (CON=) cm^{-1}; NMR δ 2.96 (d, J = 15 Hz, 1, NCHHAr), 3.37 (diffuse dd, J = 6.25 and 10 Hz, 1, C(7a)H), 4.95 (d, J = 15 Hz, 1, NCHHAr), 5.97 (s, 2, OCH_2O), 6.58–6.88 (m, 5, aromatic H), 7.15–7.30 (m, 3, aromatic H). Anal. Calcd for $C_{22}H_{23}NO_3$: C, 75.62; H, 6.63; N, 4.01. Found: C, 75.68; H, 6.52; N, 4.09.

(±)-α-Lycorane (1). A mixture of **20** (349 mg) and $LiAlH_4$ (157 mg) in anhydrous ether–THF (1:1) (66 mL) (freshly distilled from $LiAlH_4$) was refluxed with stirring for 40 min. Excess of $LiAlH_4$ was decomposed at 0–5 °C with saturated aqueous Na_2SO_4 (4 mL) and a precipitate was filtered. The precipitate was washed well with ether and the combined organic layer was dried ($MgSO_4$). Evaporation of the solvent gave an oily residue. A mixture of the residue, 2% aqueous $PdCl_2$ (6.8 mL), concentrated HCl (1 mL), and active carbon (320 mg) in C_2H_5OH (20 mL) was shaken in a Parr hydrogenation apparatus (hydrogen pressure of 80 psi) at room temperature for 87 h. Usual workup of the mixture gave 219.1 mg of an oil, whose NMR spectrum showed no signals due to the benzyl group. A mixture of the crude residue, $KHCO_3$ (163 mg)–H_2O (2.3 mL), 37% formalin (3.5 ml), and concentrated HCl (1.6 mL) in CH_3OH (11.6 mL) was refluxed for 45 min. To the mixture was added concentrated HCl (1.6 mL) and refluxing was continued for 45 min. The same treatment as noted above gave 208.9 mg of an oil, which was chromatographed over Al_2O_3 (Grade II–III) (Merck Co., Ltd.) (12 g). Elution with benzene–*n*-hexane (24:1) gave 128 mg (50%) of (±)-α-lycorane (**1**), mp 85–92.5 °C, which was recrystallized from petroleum ether to yield 30 mg (11.7%) of colorless prisms, mp 95.5–97 °C. This was identical in all respects with an authentic sample[2b] (mp 96–97.5 °C), which was kindly provided by Drs. K. Kotera and Y. Hamada.

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Registry No.—**1**, 63814-02-8; **3**, 63797-13-7; **5**, 63784-87-2; **8**, 63765-06-0; **9**, 63765-07-1; **10**, 63765-08-2; **11**, 63765-09-3; **12**, 63814-03-9; **13**, 63765-10-6; **14**, 63765-11-7; **14** pyrrolidine enamine, 63765-12-8; **15**, 63765-13-9; **17**, 63765-14-0; **20**, 63765-15-1; cyclohexanone, 108-94-1; 5-bromobenzo-1,2-dioxole, 2635-13-4; pyrrolidine, 123-75-1; benzylamine, 100-46-9.

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Behavior and Stability of Catalysts in Bi- and Triphase Transfer Catalysis

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Phase-transfer catalysis is becoming an increasingly important technique in organic synthesis.[2-7] However, very little is known about the behavior of the catalysts under biphase[2-6] and triphase conditions.[7]

Recently we observed that alkylation of thio reagents, by alkyl halides of low reactivity, gave poor yields (<20%) under biphasic conditions. Furthermore, with triphase systems, the repeatability of the reaction with the same catalyst (anion exchange resin) was not maintained after three runs.[8]

These facts prompted us to examine the chemical behavior, in classical PTC media, of various catalysts and anions (obtained from phenylacetonitrile, imidazole, phenol, thiophenol, and octylmercaptan) in the absence of alkylating reagent.

Under biphase catalysis conditions the catalysts used were: TEBA-Cl, TBAB, and CTAB.[9] The results, presented in Table I, show that the catalyst may be decomposed by alkylating the anion. This decomposition depends upon the nature of the anion and the structure of the ammonium catalyst. With TEBA-Cl and thiophenoxide this corresponds to 93% of the concentration of the catalyst. The results obtained are consistent with a nucleophilic substitution where the anion is the nucleophile and the tertiary amine is the leaving group (Scheme I). This is analogous to the dealkylation reactions of quaternary ammonium salts by nucleophilic sulfur reagents[11] or soft nucleophiles.[12,19]

Under triphase catalysis, the catalysts used were Dowex 1 × 8 and Dowex 11 anion exchange resins. Both resins are of the trimethylbenzylammonium type (Scheme II). During the reaction the gas evolved (a volatile amine if dequaternization occurred according to Scheme I) was trapped in a saturated solution of picric acid in ethanol. The results obtained show that without anion and for a reaction time of 6 h no picrate was formed, but with the anions of thiophenol and phenylacetonitrile a picrate did form.[10]

Although the decomposition of the quaternary ammonium catalyst (Scheme I) is in most cases only a secondary reaction, it can become more important for soft nucleophiles ($RS^- >$

Scheme I

$$Nu^- + RCH_2N^+R'_3\ X^- \xrightarrow{PTC} NuCH_2R + NR'_3 + X$$

Scheme II