tosylate (20 mg) in refluxing 95% EtOH for 1 h. After removal of the solvent in vacuo, the material was dissolved in CH_2Cl_2 and shaken with H_2O and dried (Na_2SO_4). Solvents were again evaporated in vacuo, and the residue was treated with 1% Et_3N in anhydrous MeOH at reflux temperature for 1 h to give crude **10**. This material was then eluted from silica gel (4 g) by using 20% EtOAc in Et_2O to give 23 mg (19%) of neosolaniol identical by GC and NMR with an authentic sample.

T-2-Toxin (11). To a solution of **7** (50 mg, 0.12 mmol), $(C_6H_5)_3P$ (59 mg, 0.24 mmol), and isovaleric acid (25 mg, 0.25 mmol) in anhydrous THF (1.5 mL) was slowly (1 h) added a solution of diethyl azodicarboxylate (42 mg, 0.24 mmol) in THF (1.5 mL). After being stirred at room temperature for an additional 2 h, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and shaken with a saturated solution of $NaHCO_3$ (5 mL). After removal of the dried (Na_2SO_4) solvent in vacuo, the residue was passed through a clean-up column (silica gel, 1 g) by using 50% Et_2O in hexanes to remove unchanged starting material and $(C_6H_5)_3PO$. The partially purified eluate was then refluxed with pyridinium tosylate (20 mg) in 95% EtOH (5 mL) for 1 h. Removal of the solvent in vacuo gave the crude product, which was purified by elution from silica gel (2 g) with 50% Et_2O in hexanes to yield 15 mg (25%) of T-2 toxin (**11**) identical by GC and NMR with an authentic sample.

T-2 toxin (**11**) could also be obtained in 30% yield from 4β,15-diacetoxyscirpene-3α,8β-diol (**6**) by use of the above procedure without protecting the 3α-hydroxy function.

3'-Hydroxy T-2 Toxin (12). To a solution of **7** (80 mg, 0.17 mmol), $(C_6H_5)_3P$ (80 mg, 0.34 mmol), and 3-hydroxy-3-methylbutanoic acid[8] (40 mg, 0.34 mmol) in anhydrous THF (2 mL) was slowly (1 h) added a solution of diethyl azodicarboxylate (50 mg, 0.34 mmol) in THF (1 mL). After being stirred at room temperature for an additional 3 h, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and shaken with a saturated solution of $NaHCO_3$ (5 mL). After removal of the dried (Na_2SO_4) solvent in vacuo, the residue was passed through a clean-up column (silica gel, 2 g) by using Et_2O to remove unchanged starting material and $(C_6H_5)_3PO$. The partially purified eluate was then refluxed with pyridinium tosylate (20 mg) in 95% EtOH (5 mL) for 1 h. Removal of the solvent in vacuo gave the crude product, which was purified by elution from silica gel (2 g) with Et_2O to give 17 mg (21%) of 3'-hydroxy T-2 toxin (**12**), whose spectral properties (IR and ^1H NMR) were identical with those reported.[8] Required for $C_{24}H_{34}O_{10}$ m/z 482.2152, found m/z 482.2149.

3α-(2-Tetrahydropyranyloxy)-15-acetoxyscirpene (13). To a solution of **4**[4] (250 mg, 0.62 mmol) and (*N*,*N*-dimethylamino)pyridine (293 mg, 2.4 mmol) in anhydrous CH_3CN (4 mL) was added phenyl chlorothionocarbonate (344 mg, 2.0 mmol). After being stirred at room temperature for 3 h, the reaction mixture was diluted with Et_2O (50 mL) and shaken with H_2O (3 × 20 mL). After removal of the dried (Na_2SO_4) solvent in vacuo, the crude residue was eluted from a silica gel (5 g) column with 40% Et_2O in hexanes to yield 193 mg of thionocarbonate, which was used as such in the next step.

To a solution of the above material in anhydrous toluene (8 mL) was added α,α'-azobisisobutyronitrile (62 mg, 0.38 mmol) and tri-*n*-butyltin hydride (420 mg, 1.44 mmol). After refluxing for 0.5 h, the solvent was removed in vacuo. The residue was eluted from silica gel (5 g) with 50% Et_2O in hexanes to yield 134 mg (56%) of **13** as a mixture of diastereomers: IR 1735 cm^{-1}; NMR δ 0.81, 0.82* (s, 3, H-14), 0.91, 0.94* (d, 2, J = 7 Hz, H-4), 1.72, 1.73* (s, 3, H-16), 2.05 (s, 3, OAc), 2.84 (d, 1, J = 4 Hz, H-13), 3.06, 3.07* (d, 1, J = 4 Hz, H-13), 5.45, 5.47* (d, 1, J = 6 Hz, H-10). Molecular ion was not observed; required for M^+ - THP ($C_{17}H_{23}O_5$) m/z 307.1545, found m/z 307.1543.

3α-(2-Tetrahydropyranyloxy)scirpen-15-ol (14). To a cold (0 °C) solution of **13** (113 mg, 0.29 mmol) in MeOH (3 mL) and THF (7 mL) was added cold (0 °C) aqueous NaOH (0.3 N, 10 mL). After standing at 5 °C for 18 h, the reaction mixture was diluted with H_2O (50 mL) and extracted with $CHCl_3$ (3 × 50 mL). The combined organic layers were washed with H_2O and dried (Na_2SO_4). Removal of the solvent in vacuo yielded 95 mg (95%) of the THP ether **14** as a mixture of diastereomers: IR 3600 cm^{-1}; NMR δ 0.90, 0.92* (d, 2, J = 7 Hz, H-4), 0.91 (s, 3, H-14), 1.73, 1.74* (s, 3, H-16), 2.84, 2.85* (d, 1, J = 4 Hz, H-13), 3.06, 3.07* (d, 1, J = 4 Hz, H-13), 3.52 (m, 2, H-15), 5.46, 5.51* (d, 1, J = 4 Hz, H-10). Molecular ion was not observed; required for M^+ - THP ($C_{15}H_{21}O_4$) m/z 265.1440, found m/z 265.1436.

3α-(2-Tetrahydropyranyloxy)-15-(formyloxy)scirpene (15). To a solution of **14** (90 mg, 0.26 mmol) in anhydrous pyridine (2 mL) was added formylimidazole (180 mg, 2 mmol). After the mixture was stirred at room temperature for 4 h, the solvent was removed in vacuo. The resulting residue was dissolved in $CHCl_3$ (20 mL) and washed with H_2O (2 × 10 mL) and dried (Na_2SO_4). Removal of the solvent in vacuo yielded 96 mg (98%) of the THP ether **15** as a mixture of diastereomers: IR 1735 cm^{-1}; NMR δ 0.82, 0.83* (s, 3, H-14), 0.90, 0.92* (d, 2, J = 7 Hz, H-4), 1.73 (s, 3, H-16), 2.84 (d, 1, J = 4 Hz, H-13), 3.06, 3.07* (d, 1, J = 4 Hz, H-13), 3.94 (d, 1, J = 12 Hz, H-15), 4.21 (d, 1, J = 12 Hz, H-15), 5.46, 5.50* (d, 1, J = 6 Hz, H-10), 8.06 (s, 1, formyl). Molecular ion was not observed; required for M^+ - THP ($C_{16}H_{21}O_5$) m/z 293.1389, found m/z 293.1387.

3α-(2-Tetrahydropyranyloxy)-15-(formyloxy)scirpen-8β-ol (16). A solution of **15** (90 mg, 0.24 mmol) and SeO_2 (36 mg, 0.32 mmol) in dioxane (7 mL) containing H_2O (0.3 mL) was refluxed for 18 h. The solvents were removed in vacuo, and the residue eluted from silica gel (5 g) with 50% EtOAc in hexanes to yield 30 mg (32%) of the THP ether **16** as a mixture of diastereomers: IR 3600, 1735 cm^{-1}; NMR δ 0.75, 0.76* (s, 3, H-14), 0.83, 0.86* (d, 2, J = 7 Hz, H-4), 1.76 (s, 3, H-16), 2.81 (d, 1, J = 4 Hz, H-13), 3.01, 3.02* (d, 1, J = 4 Hz, H-13), 5.48 (m, 1, H-10), 7.99 (s, 1, formyl). Molecular ion was not observed; required for M^+ - THP ($C_{16}H_{21}O_6$) m/z 309.1338, found m/z 309.1342.

Sporotrichiol (17). To a stirred solution of **16** (25 mg, 0.06 mmol), $(C_6H_5)P$ (31 mg, 0.12 mmol), and isovaleric acid (12 mg, 0.12 mmol) in anhydrous THF (0.2 mL) was slowly (1 h) added a solution of diethyl azodicarboxylate (16 mg, 0.12 mmol) in THF (0.2 mL). After the mixture was stirred at room temperature for an additional 3 h, the solvent was removed in vacuo, and the residue eluted from a silica gel column (1 g) with Et_2O to remove $(C_6H_5)_3PO$. This partially purified material was refluxed with pyridinium tosylate (20 mg) in 95% aqueous MeOH (5 mL) for 20 h. Removal of the solvent gave the crude product, which was purified by elution from silica gel (1 g) with 20% hexanes in Et_2O to yield 4 mg (22%) of sporotrichiol (**17**), whose spectral properties (IR, ^1H NMR, and HRMS) were identical with those reported.[7]

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Detection of an Azomethine Ylide and Its Conversion to Aziridine

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The thermal ring opening of substituted aziridines to stabilized azomethine ylides has been extensively studied.[1-3] The reverse reaction is implicit in those cases where aziridine cis/trans equilibration occurs[3] and possibly also in the reactions of diazoalkanes with imines,[4] but we are not aware of previous examples where an ester-stabilized

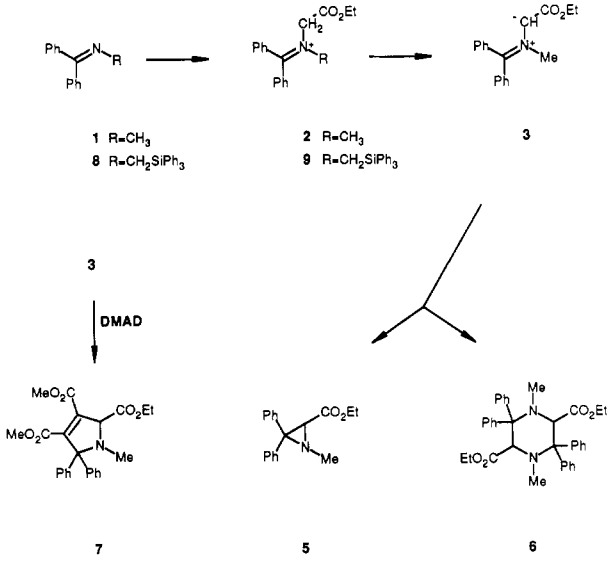
(1) Heine, H. W.; Peavy, R. E. *Tetrahedron Lett.* **1965**, 3123.
(2) Padwa, A.; Hamilton, L. *Tetrahedron Lett.* **1965**, 4363. Huisgen, R.; Scheer, W.; Szeimeis, G.; Huber, H. *Ibid.* **1966**, 397.
(3) Huisgen, R.; Scheer, W.; Huber, H. *J. Am. Chem. Soc.* **1967**, *89*, 1753. Hermann, H.; Huisgen, R.; Mäder, H. *Ibid.* **1971**, *83*, 1779.
(4) For recent examples, see: Bartnik, R.; Mloston, G. *Tetrahedron* **1984**, *40*, 2569.

0022-3263/87/1952-3470$01.50/0

azomethine ylide can be generated independently and shown to undergo electrocyclic ring closure to the aziridine.[5]

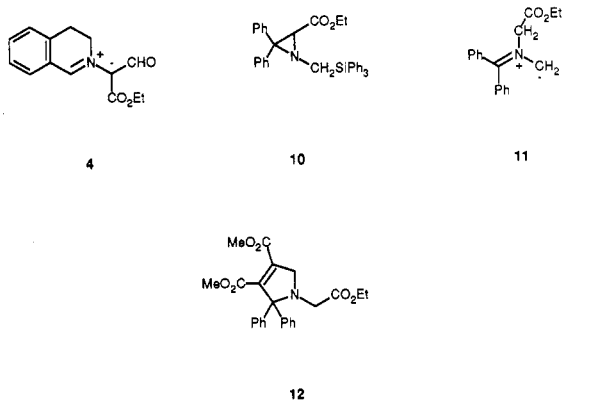
Alkylation of imine 1[6] with $CF_3SO_3CH_2CO_2Et$[7] gave the crystalline iminum salt **2** in greater than 90% yield. Upon treatment with KO-*t*-C_4H_9 in tetrahydrofuran at −70 °C, **2** was rapidly transformed into the bright red ylide **3**. Extensive line broadening at temperatures where **3** was stable precluded unambiguous interpretation of the NMR spectra of solutions containing **3**. However, the UV λ_{max} (THF) at 457 nm (ϵ ca. 280) was easily observed. This compares well with the reported UV spectrum for the highly stabilized **4** and related structures.[8]

Warming the solution of ylide above ca. −20 °C resulted in gradual fading of the red color. Depending on the concentration and rate of warming, 10–20% yields of the aziridine **5** could be isolated, together with a dimer (tentatively, **6**[9]) and complex polar side products. On the



other hand, addition of dimethyl acetylenedicarboxylate (DMAD) at −70 °C followed by warming to room temperature afforded the 2 + 3 cycloadduct **7** in 87% yield. Apparently, dipole generation was efficient, but electrocyclic ring closure was not fast at −20 °C. Accordingly, the conversion of **3** into **5** was reexamined under "temperature shock–dilution" conditions. Thus, dropwise transfer (cannula) of cold **3** in THF (−78 °C) into a reservoir of toluene containing 4 equiv of pyridine at 100 °C gave **5** in 78% yield. Aziridine decomposition, perhaps due to surface catalysis by the glass reaction vessel, was a problem if the pyridine additive was omitted.

A second example was studied where the behavior of stabilized and nonstabilized ylides could be compared. Thus, *N*-triphenylsilyl imine 8[10] was alkylated with $CF_3SO_3CH_2CO_2Et$ (24 h, CH_2Cl_2) to afford **9**. Treatment of crude (noncrystalline) **9** with KO-*t*-C_4H_9 at −70 °C in THF again resulted in a deep red color, but the temperature shock–dilution technique gave complex products from which the aziridine **10**[11] could not be isolated. When **9** was exposed to CsF under the conditions for generation of nonstabilized azomethine ylides,[12,13] no aziridine derivatives could be detected. However, if the experiment was performed in the presence of DMAD, two products of 2 + 3 cycloaddition were isolated. The minor product (8%) proved to be identical with **7** while the major product was the isomer **12** derived from nonstabilized ylide **11**. Thus, **11** undergoes relatively little equilibration with the presumably more stable **3**.



Comparison of the two series of experiments shows that stabilized azomethine ylide **3** does undergo electrocyclic ring closure, but with a significant thermal barrier. This is consistent with the pioneering studies of Huisgen et al. where the azomethine ylides were generated by flash photolysis.[3] No evidence for aziridine formation from nonstabilized ylide **11** has been found, as in previous studies of the desilylation process.[12,13] Since there are examples of such cyclizations from nonstabilized ylides generated by strong base techniques,[14] the absence of aziridines in the desilylation experiments is probably not due to any lack of dipole reactivity. More likely, the dipoles are scavenged too rapidly by potential dipolarophiles such as the starting iminium salt; aziridine formation is simply too slow to compete. Dipole 2 + 3 cycloaddition, on the other hand, is a fast reaction for both the stabilized **3** and the nonstabilized **11**.

In conclusion, detection of a reactive azomethine ylide **3** and its electrocyclic ring closure to **5** are demonstrated. The nonstabilized ylide **11** can be generated by the desilylation technique without extensive equilibration to the stabilized isomer **3**.

Experimental Section

1-Carbethoxy-*N*-methyl-*N*-(diphenylmethylene)methanaminium Trifluoromethanesulfonate (2). Carbethoxymethyl trifluoromethanesulfonate[7] (2.36 g, 10.0 mmol) was added neat to a stirred solution of imine 1[6] (1.95 g, 10.0 mmol) in acetonitrile (3 mL) cooled to 0 °C. The reaction was allowed to warm to room temperature and stir for 2 h. Removal of the solvent under

(5) Detection or isolation of azomethine ylides: Huisgen, R.; Niklas, K. *Heterocycles* **1984**, *22*, 21. Seidl, H.; Huisgen, R.; Knorr, R. *Chem. Ber.* **1969**, *102*, 904. Fleury, J.-P.; Schoeni, J.-P.; Clevin, D.; Fritz, H. *Helv. Chim. Acta* **1975**, *58*, 2018.

(6) Moretti, I.; Torre, G. *Synthesis* **1970**, 141.

(7) Vedejs, E.; Engler, D. A.; Mullins, M. J. *J. Org. Chem.* **1977**, *42*, 3109.

(8) Reference 5 reports λ_{max} 456 nm (benzene) for compound **4**.

(9) **6**: oil after PTLC over silica gel, R_f 0.45 (9:1 hexane/ethyl acetate); partial NMR ($CDCl_3$) ppm 3.58 (2 H, s, NCH), 1.80 (6 H, s, NCH_3); MS, *m/e* 562.2831 (calcd for $C_{36}H_{38}N_2O_4$, 582.28313); an alternative head to head dimer structure would require adjacent, quaternary (phenyl substituted) carbons. In analogous head to head dimers, the chemical shift of NC*H* is more than 1 ppm downfield of the corresponding signals of **6**; Huisgen, R.; Scheer, W.; Szeimies, G.; Huber, H. *Tetrahedron Lett.* **1966**, 397.

(10) Hullot, P.; Cuvigny, T. *Bull. Chim. Soc. Fr.* **1973**, 2989.

(11) NMR signals at δ 3.07 (s) and 3.85–4.15 (m) could have been due to **10**, but attempted purification lead to decomposition.

(12) Vedejs, E.; Martinez, G. R. *J. Am. Chem. Soc.* **1979**, *101*, 6452.

(13) See Vedejs and West [Vedejs, E.; West, F. G. *Chem. Rev.* **1986** *86*, 941] for references to related studies by K. Achiwa, A. Padwa, T. Livinghouse, O. Tsuge, and co-workers.

(14) Deyrup, J. A.; Szabo, W. A. *J. Org. Chem.* **1975**, *40*, 2048. Takayama, H.; Nomoto, T., *J. Chem. Soc., Chem. Commun.* **1982**, 408. Beugelmans, R.; Benadijila-Iguertsira, L.; Chastanet, J.; Negron, G.; Roussi, G. *Can. J. Chem.* **1985**, *63*, 725 and references therin.

(15) **Note Added in Proof**: A related example for aziridine formation has recently been described: McCarthy, J. R.; Barney, C. L.; O'Donnell, M. J.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1987**, 469.

reduced pressure left an oil, which slowly solidified upon standing. The resulting solid was triturated with ether and filtered under a dry nitrogen purge to give to a white solid (4.21 g, 97%): mp 73 °C; IR ($CHCl_3$) 2995 (m), 1750 (s), 1615 (m), 1597 (m), 1452 (s), 1350 (s), 1275 (s), 1225 (s), 1162 (m), 1028 (s) cm^{-1}; NMR ($CDCl_3$, 270 MHz) 7.90–7.20 (m, 10 H), 4.96 (s, 2 H), 4.33 (q, J = 7 Hz, 2 H), 3.95 (s, 3 H), 1.32 (t, J = 7 Hz, 3 H).

2-Carbethoxy-1-methyl-3,3-diphenylaziridine (5). 1-Carbethoxy-*N*-methyl-*N*-(diphenylmethylene)methanaminium trifluoromethanesulfonate (**2**) (138 mg, 0.32 mmol) was dissolved in tetrahydrofuran (3.2 mL) at room temperature and then cooled to −78 °C. To this homogenous solution was added potassium *tert*-butoxide (0.89 mL, 0.36 M in THF, 0.32 mmol) via syringe. The resultant deep red solution was stirred at −78 °C for 40 min and then added dropwise, via cannula, to a heated (102 °C) stirring solution of pyridine (0.10 mL, 1.24 mmol) in toluene (9.0 mL). The addition required approximately 8 min to complete, after which time the reaction was heated for an additional 30 min. The reaction mixture was cooled and the solvents were removed in vacuo. The residue was dissolved in ether and filtered through a glass wool plug. The ether was removed by rotary evaporation and the resultant orange oil was purified via column chromatograph [silica gel, hexanes/ethyl acetate, 4:1 (v/v)] to afford benzophenone (10 mg, 17%) and then the desired aziridine **5** as a clear oil (70 mg, 78%, R_f 0.2): IR ($CHCl_3$) 3020 (w), 2975 (m), 1740 (s), 1470 (m), 1450 (m), 1300 (m), 1270 (s), 1185 (s) cm^{-1}; NMR ($CDCl_3$, 270 MHz) 7.40–7.18 (m, 10 H), 4.00–3.85 (m, 2 H), 3.03 (s, 1 H), 2.28 (s, 3 H), 0.85 (t, 3 H, J = 7.1 Hz); MS (m/z) 281 (M^+), 55 (base); exact mass calcd for $C_{18}H_{19}NO_2$ 281.14157, obsd 281.1418 (0.8 ppm error).

2-Carbethoxy-3,4-dicarbomethoxy-1-methyl-5,5-diphenyl-3-pyrroline (7). Potassium *tert*-butoxide (1.90 mL, 0.53 M in THF, 1.00 mmol) was added to a suspension of iminium salt **2** (431 mg, 1.00 mmol) in THF (10 mL) at −78 °C. The resulting deep red solution was stirred for 5 min after which time dimethyl acetylenedicarboxylate (135 μL, 142 mg, 1.00 mmol) was added and the reaction was allowed to warm to room temperature over 1 h. The solvent was removed by rotary evaporation and the residue was subjected to silica plug filtration using ether as the eluent. Purification of the resultant oil by PTLC (silica gel, 20% ethyl acetate/hexane) afforded pyrroline **7** (360 mg, 87% R_f 0.23) as an oil: IR ($CHCl_3$) 3000 (m), 2945 (m), 1742 (s), 1736 (s), 1440 (m), 1285 (s), 901 (s) cm^{-1}; NMR ($CDCl_3$, 270 MHz) 7.68–7.08 (m, 10 H), 4.37 (s, 1 H), 4.24 (q, J = 7 Hz, 2 H), 3.76 (s, 3 H), 3.50 (s, 3 H), 1.99 (s, 3 H), 1.27 (t, J = 7 Hz, 3 H); MS (m/z) 423 (M^+), 350 (base); exact mass calcd for $C_{24}H_{25}NO_6$ 423.16816, obsd 423.1680 (−0.4 ppm error).

1-(Carbethoxymethyl)-3,4-dicarbomethoxy-2,2-diphenyl-3-pyrroline (12). Carbethoxymethyl trifluoromethanesulfonate (95 μL, 130 mg, 0.55 mmol) was added to a solution of imine **8** (250 mg, 0.55 mmol) in methylene chloride (600 μL). After 24 h, the solvent was removed under a dry stream of nitrogen and replaced with acetonitrile (4 mL). Dimethyl acetylenedicarboxylate (68 μL, 78 mg, 0.55 mmol) was added to this solution, which was then transferred by cannula into a flask containing anhydrous cesium fluoride (662 mg, 4.36 mmol). After stirring at ambient temperature for 23 h, the solvent was removed by rotary evaporation and the residue was subjected to a silica pork workup. The crude product was purified by PTLC (silica gel, 20% ethyl acetate/hexane) to give cycloadducts **12** (117 mg, 52%, R_f 0.22) and **7** (19 mg, 8%, R_f 0.14). Cycloadduct **12**: IR ($CHCl_3$) 3025 (m), 3000 (m), 2955 (m), 2900 (w), 2850 (w), 2790 (w), 1730 (s), 1670 (m), 1490 (m), 1445 (s), 1370 (m), 1272 (s), 1210 (s), 1192 (s), 1110 (m), 1080 (m), 1030 (m), 970 (m), 905 (w), 855 (w), 790 (w), 695 (m) cm^{-1}; NMR ($CDCl_3$, 270 MHz) 7.40 (m, 10 H), 4.10 (q, J = 7 Hz, 2 H), 4.06 (s, 2 H), 3.80 (s, 3 H), 3.52 (s, 3 H), 2.91 (s, 2 H), 1.20 (t, J = 7 Hz, 3 H); MS (m/z) 423 (M^+); exact mass calcd for $C_{24}H_{25}NO_6$ 423.16815, obsd 423.1680 (−0.4 ppm error).

Acknowledgment. This work was supported by the National Institutes of Health (CA17918 and RRO-2238-01 for the AM-500 NMR system).

Registry No. **1**, 13280-16-5; **2**, 108795-80-8; **3**, 108795-81-9; **5**, 108795-82-0; **6**, 108795-83-1; **7**, 108795-84-2; **8**, 51411-41-7; **9**, 108795-86-4; **11**, 108795-87-5; **12**, 108795-88-6; DMAD, 762-42-5; $CF_3SO_3CH_2CO_2Et$, 61836-02-0.

Hyper-Acyloin Condensation, from Simple Aromatic Esters to Phenanthrenequinones: A New Reaction of C_8K

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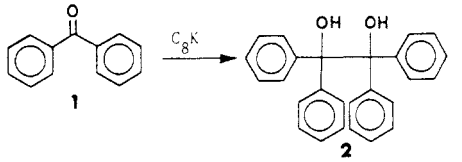
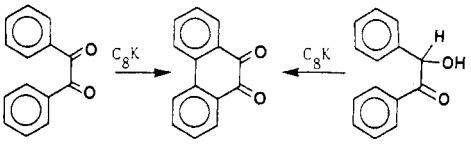
Introduction

Potassium–graphite intercalation compound, C_8K, is a useful and efficient reducing agent. In this compound potassium atoms are located in a highly ordered mode between the carbon layers of graphite. This structural feature enables a selective reactivity of C_8K, in comparison to nonintercalated dispersed potassium.[1] For example, benzophenone (**1**) undergoes a bimolecular reduction process with C_8K to form the corresponding pincaol (**2**). A "layer edgel mechanism" has been suggested to explain this specific behavior[2] (eq 1).



(1)



(2)

Recently, we reported a unique ring-closure process that occurs in the reaction of C_8K with benzil (**3**) to yield phenanthrenequinone (**4**)[3] (eq 2). In this reaction, formation of the benzil dianion (3^{2-}) is followed by a pericyclic cyclization. The resulting dianion 4^{2-} is quenched by water, and upon air oxidation phenanthrenequinone (**4**) is obtained. The same product is obtained when C_8K is reacted with benzoin (**5**). In this case, the first step is deprotonatin followed by enolization to form benzil dianion (3^{2-}), and following the sequence mentioned above phenanthrenequinone is produced[4] (eq 2). The high efficiency of this ring-closure reaction can be rationalized by the positioning of 3^{2-} in a syn conformation. This conformation can be achieved by a linkage of the dianion to the intercalate layer edge[2] (Figure 1).

Aromatic acid esters, e.g., methyl benzoate, undergo an acyloin condensation reaction with alkali metals to form a benzoin derivative.[5] However, this condensation usually gives low yields and generally is not considered an attractive synthetic method. Furthermore, the mechanism is not well established, although it is usually assumed that an α-diketone is an intermediate.

Results and Discussion

In view of the above-mentioned reactions of benzo-

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(2) Tamarkin, D.; Rabinovitz, M. *Synth. Met.* **1982**, *4*, 299.
(3) Tamarkin, D.; Benny, D.; Rabinovitz, M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 642.
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(5) General references on the acyloin condensation: Finley, K. T. *Chem. Rev.* **1964**, *64*, 573. Smith, B. H. *Bridged Aromatic Compounds*; Academic: New York, 1964; p 27. Bloomfield, J. J.; Nelke, J. M. *Org. React. (N.Y.)* **1976**, *23*, 250.

0022-3263/87/1952-3472$01.50/0