Tetrahedron Letters, Vol.31, No.26, pp 3695-3698, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

BASE-PROMOTED ELIMINATIVE CYCLIZATION: NOVEL SYNTHESIS OF FUNCTIONALIZED TETRACYCLO[6.2.1.$0^{2,7}$.$0^{4,10}$]UNDECANE AND TETRACYCLO[5.3.0.$0^{2,6}$.$0^{5,9}$]DECANE SYSTEMS

Suresh Chander Suri
University of Dayton Research Institute, c/o Air Force Astronautics Laboratory/LSX
Edwards Air Force Base, CA 93523 U.S.A.

Treatment of 1,8,9,10-tetrachloro-3α,6α-dihydroxy-11,11-dimethoxytricyclo[6.2.1.$0^{2,7}$]undec-4,9-diene (**2**) and 1,7,8,9-tetrachloro-3α-hydroxy-10,10-dimethoxytricyclo[5.2.1.$0^{2,6}$]dec-4,8-diene (**8**) with potassium-t-butoxide-t-buanol furnished 1,8,10-trichloro-11,11-dimethoxy-3α-hydroxytetracyclo[6.2.1.$0^{2,7}$.$0^{4,10}$]undec-5-ene-9-one (**3**) and 1,7,9-trichloro-8,8-dimethoxytetracyclo[5.3.0.$0^{2,6}$.$0^{5,9}$]dec-3-en-10-one (**9**) respectively via base eliminative cyclization.

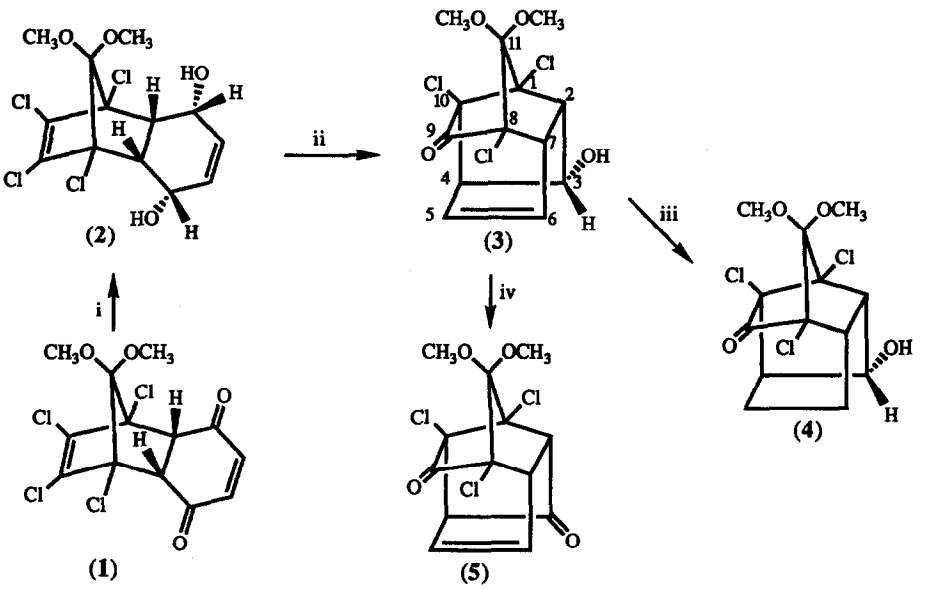
Very limited attention has been focused on the chemistry of abundantly available 1,2,3,4-tetrachloro-1,4,4a,8a-tetrahydro-9,9-dimethoxy-endo-1,4-methanonaphthalene (**1**) and its derivatives in the literature.[1-4] Herein, an efficient synthesis of new tetracyclic systems is reported from 1,8,9,10-tetrachloro-3α,6α-dihydroxy-11,11-dimethoxytricyclo[6.2.1.$0^{2,7}$]-undec-4,9-diene[5] (**2**), and from 1,7,8,9-tetrachloro-3α-hydroxy-10,10-dimethoxytricyclo-[5.2.1.$0^{2,6}$]dec-4,8-diene (**8**) via base-induced eliminative cyclization.

When a solution of **2** in butanol was treated with potassium-t-butoxide, a single product **3** was isolated in 84% yield after aqueous workup. Its infrared spectrum showed a characteristic absorption for its bridged ketone at 1791 cm^{-1} and a broad hydroxyl absorption at 3441 cm^{-1}. The presence of the ketal group was reflected by NMR signals at δ_H 3.71(3H) , 3.55(3H) and at δ_C 99.2. These observations indicated that one hydroxy group has changed to the ketone group during the course of transformation under basic conditions. The up-field signal at δ_C 193.3 of the carbonyl carbon revealed its interaction with the double bond and/or the lone pair oxygen electrons of the ketal moiety. The former possibility was eliminated because the palladium catalyzed hydrogenated product **4** still showed an up-field carbonyl signal at δ_C 195.8. It was desired to determine if the relative positions of the hydroxy group and the double bond of **2** had changed upon conversion to **3**. Thus, **3** was oxidized using PCC reagent to form **5**, which showed an olefinic resonance typical of a non-conjugated enone. The analytical and spectral data[6] of the product **3** were consistent with the structure shown in scheme-I.

To confirm the conversion of allylic hydroxy group into a bridged ketone, 1,7,8,9-tetrachloro-3α-hydroxy-10,10-dimethoxytricyclo[5.2.1.$0^{2,6}$]dec-4,8-diene (**8**) was prepared via the illustrated reaction sequence as shown in scheme-II. 1,7,8,9-Tetrachloro-10,10-dimethoxytricyclo[5.2.1.$0^{2,6}$]dec-8-en-3-one (**6**) was prepared according to a recent

published procedure.[7] Treatment of a benzene solution of 6 with benzeneselenic

Scheme-I



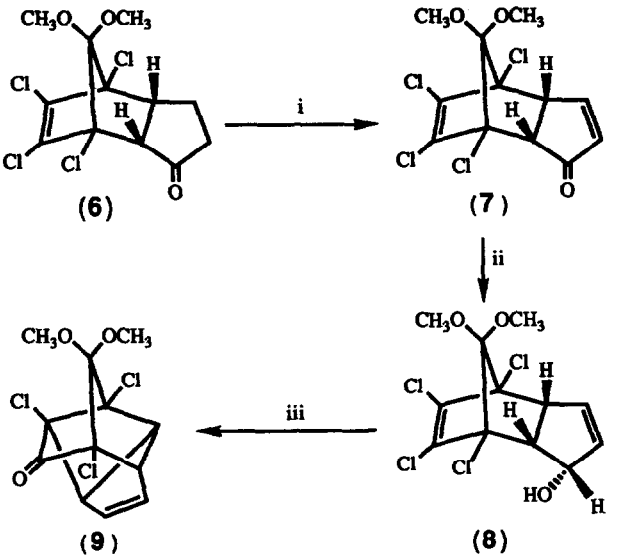
Reagents and yield: i. $NaBH_4/CeCl_3/MeOH$,85%; ii. t-BuOH/t-BuOK,84%; iii. 5% Pd-C/MeOH/H_2,100%;iv.PCC/CH_2Cl_2,70%.

anhydride using Barton's procedure[8] furnished enone 7, b.p. 130°C/.05mm. Enone 7 was transformed stereoselectively to endo allylic alcohol 8, m.p. 131°C, using sodium borohydride-cerium(III) chloride heptahydrate.[5,9] When 8 was treated with t-butanol/potassium t-butoxide, it was converted to a single compound 9 in 84% yield. Its infrared spectrum showed the absence of a hydroxy stretch and the presence of a strong absorption characteristic of a bridged ketone at 1785 cm^{-1}. The presence of the dimethoxyketal group was confirmed by an NMR resonances at δ_H 3.66(3H), 3.55(3H) and δ_C 106.2. One can undoubtedly infer from this experiment that the hydroxy group has been converted to a bridged ketone under basic conditions. The spectral and analytical data[6] were compatible with structure 9.

To account for the formation of 3, a mechanism shown in scheme-III has been postulated. The alkoxide anion attacks the electron-deficient double bond in an intramolecular fashion, thus developing a negative charge at the vicinal carbon atom. Because of the endo- geometry of the molecule, the disubstituted double bond is attacked by the vicinal carbanion, causing a 1,2 shift of the double bond followed by cleavage of the ether linkage and elimination of chloride anion to give 3. A similar mechanism is envisioned for the formation of 9 from 8 under basic conditions.

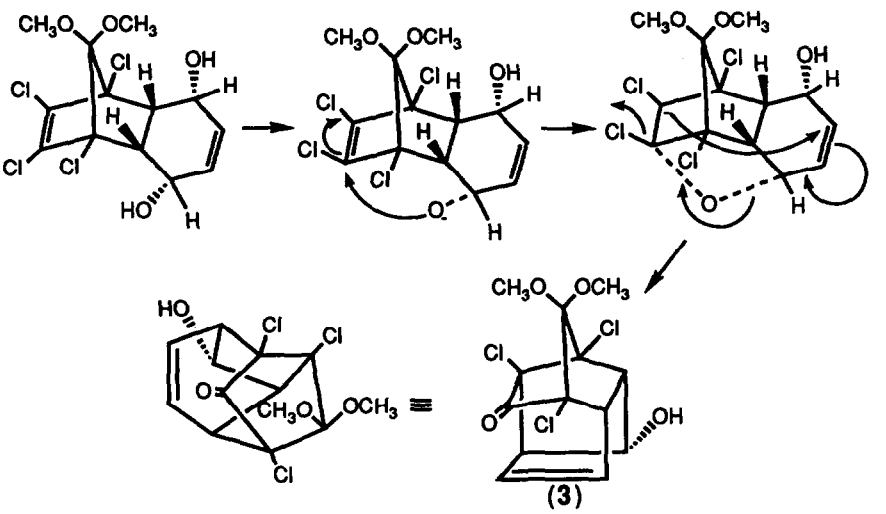
Similar results were also obtained when 2 was subjected to Winstein's procedure[10] of reductive dechlorination using sodium/tetrahydrofuran/t-butanol.

Scheme-II



Reagents and yield: i. $(C_6H_5SeO)_2O/C_6H_6$, 60%; ii. $NaBH_4/CeCl_3$, 80%; iii. t-BuOH/t-BuOK, 83.75%

Scheme-III



In spite of the fact that the spectral and analytical data are consistent with structure **3** & **2**, the possibility of other structures if any, can not be ruled out conclusively. The chemistry of **3** & **5** is being explored for the synthesis of substituted polycyclic cage compounds.

The author thanks Drs. Vijay Nair and G. K. S. Prakash for providing 300- and 200- MHz ^{1}H & ^{13}C NMR spectra. Financial support of this study by the Air Force Office of Scientific Research, Directorate of Chemical and Atmospheric Sciences, is gratefully acknowledged.

REFERENCES AND NOTES

1. P. E. Eaton, Y. S. Or, and S. J. Branca, J. Am. Chem. Soc., 1981, **103**, 2134.
2. G. Mehta and M. S. Nair, J. Am. Chem. Soc., 1985, **107**, 7519.
3. T. C. Chou, K. S. Chuang, and C. H. Lee, J. Org. Chem., 1988, **53**, 2835 and refrences cited therein.
4. A. P. Marchand and T. C. Chou, J. Chem. Soc., 1973, 1949.
5. A. P. Marchand, W.D. LaRoe, G. V. M. Sharma, S. C. Suri, and D.S. Reddy, J. Org. Chem., 1986, **51**, 1622.
6. The spectral and analytical data of selected compounds are as follows:
Compound **3**: m.p. 118 °C, IR(KBr): 3441, 2991, 2952, 1791, 1217, 1097, 890, 765, 733, 720, 698 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.43(1H, dt, J_1=7.8 Hz, J_2=1.5 Hz), 5.99(1H, m), 3.94(1H, dd, J_1=8.3 Hz, J_2=2 Hz), 3.71(3H, s), 3.55(3H, s), 3.38(1H, ddd, J_1=9.3 Hz, J_2=5.6 Hz, J_3=1.5 Hz), 3.18(1H, m), 3.09(1H, ddd, J_1=9.3 Hz, J_2=3.6 Hz, J_3= 2.2 Hz), 2.94(1H, d, J=8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.3, 137.4, 128.4, 99.2, 83.5, 83.4, 82.7, 80.1, 61.7, 54.2, 52.0, 47.8, 47.1. Analysis Calcd. for $C_{13}H_{13}Cl_3O_4$: C= 45.98, H=3.86, Cl=31.32; Found C=45.76, H=3.88, Cl= 31.67. Compound **4**: m.p. 149-50 °C; IR(KBr): 3433, 2953, 2893, 2842, 1788, 1458, 1215, 1101, 1078, 1045, 1030, 970, 889, 655 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$): δ 4.33(1H, bd, J=5.7 Hz), 3.67(3H, s), 3.56(3H, s), 3.29(1H, ddd, J_1=10.6 Hz, J_2=3.52 Hz, J_3= 1.76 Hz), 2.61-2.96(3H, m), 1.48-2.01(4H, m) ; ^{13}C NMR(22.6 MHz, $CDCl_3$): δ 195.8, 102.4, 82.9, 79.3, 78.1, 77.7, 57.7, 52.3, 52.2, 51.9, 46.2, 26.2, 15.7; GC-MS (70 ev): m/z 305(M^+-HCl). Compound **5**: m.p. 151-52°C, IR(KBr): 2953, 1798, 1770, 1206, 1145, 1110, 1090, 972, 711 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$): δ 6.42(1H, dt, J_1=8 Hz, J_2=1.65 Hz), 6.27(1H, dd, J_1=8 Hz, J_2=5.8 Hz), 3.71(3H, s), 3.6(3H, s), 3.3(1H, dd, J_1=8 Hz, J_2=5.8 Hz), 3.22(1H, dd, J_1=9.2 Hz, J_2=2.9 Hz); ^{13}C NMR(75 MHz, $CDCl_3$): δ 200.7, 191.6, 135.5, 132.8, 102.5, 83.4, 76.5, 73.5, 58.5, 53.1, 52.3, 52.1, 49.8. Analysis Calcd. for $C_{13}H_{11}Cl_3O_4$: C=46.25, H=3.28, Cl=31.5; Found C=46.28, H=3.42, Cl=31.52. Compound **2**: m.p. 125-26 °C, IR(KBr) 2949, 1785, 1218, 1207, 1122, 1093, 769, 754 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.35(1H, dd, J_1=5.7 Hz, J_2=2.6 Hz), 6.14(1H, dd, J_1=5.7 Hz, J_2=2.8 Hz), 3.66(3H, s), 3.55(3H, s), 3.39-3.71(2H, m); ^{13}C NMR(50 MHz, $CDCl_3$): 191.9, 138.9, 135, 106.2, 83.9, 74.4, 70.3, 55.7, 55.5, 53.0, 52.0, 52.1; GC-MS (70 ev): m/z= 309 (M^+).
7. E. Gossinger and R. Muller, Tetrahedron 1989, **45**, 1390.
8. D. H. R. Barton, D. J. Lester, and S. V. Ley, J. Chem. Soc. Chem. Comm., 1978, 130.
9. J. -L. Luche, L. Rodriguez-Hahn, and P. J. Crabbe, J. Chem. Soc., Chem. Comm., 1978, 601.
10. P. Bruck, D. Thompson, and S. Winstein, Chem. Ind. (London), 1960, 405; P.G. Gassman and P.G. Pape, J. Org. chem., 1964, **29**, 160.

(Received in USA 5 February 1990)