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1-BROMO-2-CHLOROCYCLOPROPENE--A NEW CYCLOPROPARENE SYNTHON. SYNTHESIS OF 1H-CYCLOPROPA[b]PHENANTHRENE

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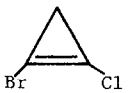
Summary: Treatment of 1-bromo-2,2-dichloro(trimethylsilyl)cyclopropane (2) with tetra-n-butylammonium fluoride in tetrahydrofuran yields 1-bromo-2-chlorocyclopropene (1). 1H-Cyclopropa[b]phenanthrene (3) can be prepared by aromatization of the Diels-Alder adduct of 1 and 1,2-dimethylene-3,5,6,7,8,9-hexahydronaphthalene (6) using DDQ followed by potassium t-butoxide in tetrahydrofuran.

Although 1,2-dichlorocyclopropene[3] has been prepared by treating tetrachlorocyclopropene with tri-n-butyltin hydride in tetraglyme, the yield is low and the use of this compound or other dihalocyclopropenes in the synthesis of cyclopropareneshas not been reported. We describe here the synthesis of 1-bromo-2-chlorocyclopropene (1), a moderately stable compound,



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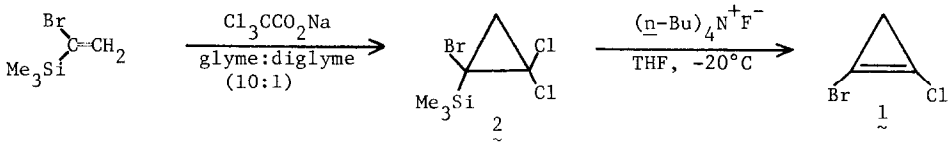
and its use in a key step of the synthesis of 1H-cyclopropa[b]phenanthrene.[4]

The starting material 2 was prepared from α-bromovinyltrimethylsilane[5] and converted to 1 by treatment with tetra-n-butylammonium fluoride.[6] Thus a suspension of α-bromovinyltrimethyl-



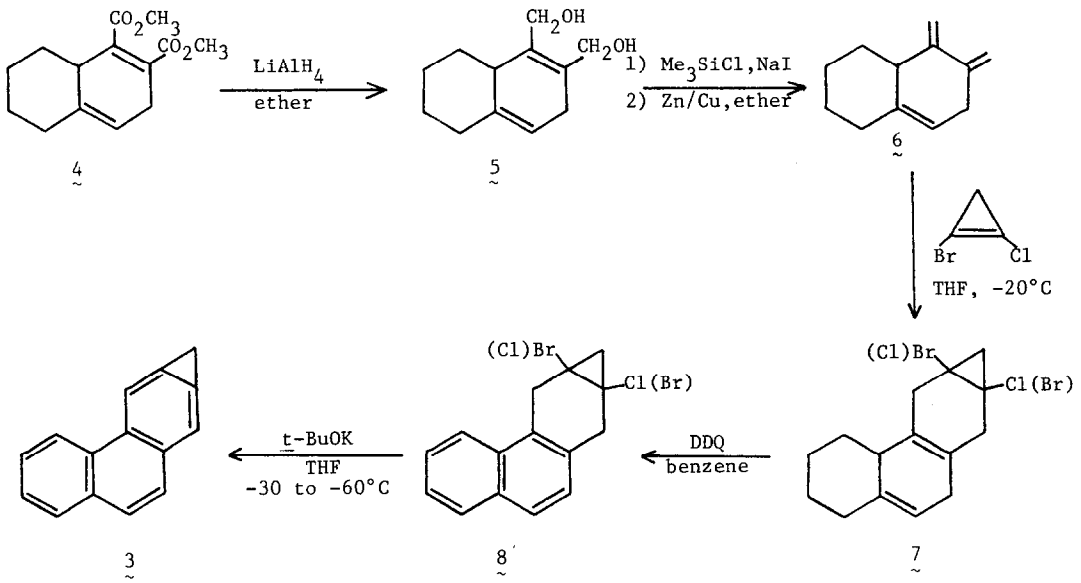
silane (34.9 g, 0.195 mol) and sodium trichloroacetate (36.2 g, 0.195 mol) in 25 ml of glyme:diglyme (10:1) was stirred under nitrogen at 80-90°C until CO_2 evolution ceased (~ 10 h). The resulting dark suspension was cooled to 25°C and diluted with n-pentane (100 ml) and water (100 ml). After stirring for 0.5 h, the mixture was filtered through glass wool and the residue washed with n-pentane (200 ml). The aqueous phase from the filtrate was then extracted

with n-pentane (150 ml) and the combined organics were washed exhaustively with water, dried over $CaCl_2$, and concentrated in vacuo. The dark residue is a mixture of starting material, glyme, and 2. The residue was then subjected to the same reaction until the starting material was nearly consumed. The product was purified by vacuum distillation, b.p. 45-48°C/0.1 mm Hg. ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.29 (s, 9 H), 1.85 (AB, 2 H, J = 8.35 Hz).

Conversion to the cyclopropene (1) was effected by adding 2 (922 mg, 0.664 ml, 3.5 mmol) to a stirred solution (1 M in THF) of tetra-n-butylammonium fluoride (3.5 ml, 3.5 mmol) at -30 to -40°C. The mixture was warmed to -20°C and stirred for 1 h. The cyclopropene[7] and other volatile materials were then removed in vacuo (0.01 mm Hg) to a liquid nitrogen trap. The ^{1}H NMR spectrum (90 MHz, THF-d_8) of 1 exhibits a singlet at δ 2.03. Elemental composition was determined by high resolution mass spectrometry: calcd for $C_3H_2{}^{79}Br^{35}Cl$ m/e 151.9028, found m/e 151.9025; calcd for $C_3H_2{}^{81}Br^{37}Cl$ m/e 155.8978, found m/e 155.8977.

The use of 1 in the synthesis of 1H-cyclopropa[b]phenanthrene (3) is illustrated in Scheme I. The immediate precursor to 3, compound 8, can be prepared from 4, the Diels-Alder

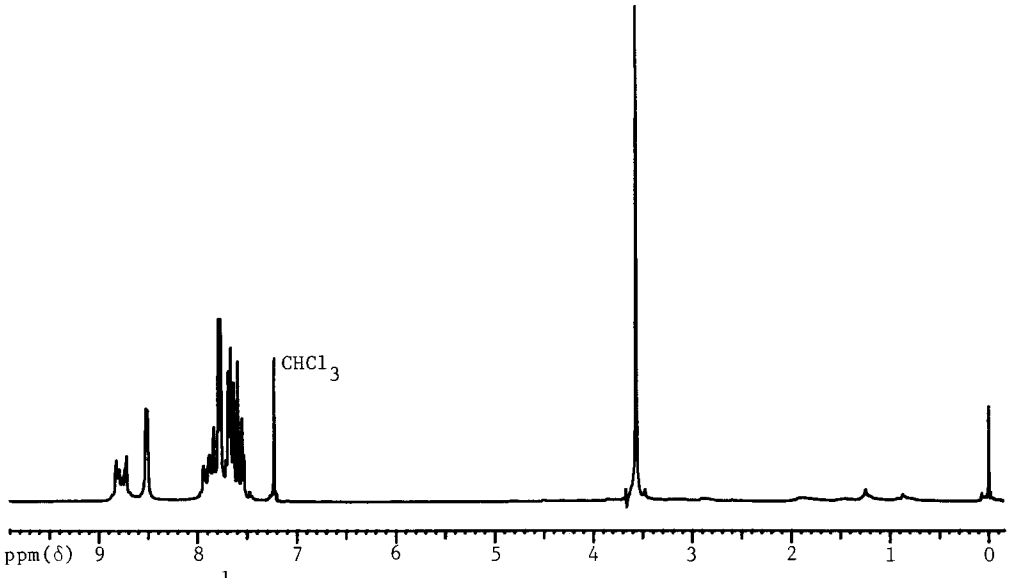
Scheme I



adduct of 1-vinylcyclohexene and dimethyl acetylenedicarboxylate.[8] The reduction of 4 using $LiAlH_4$ in ether yielded the diol 5 in 76% yield. Conversion to 6 was effected in 80% yield using the procedure of Angus and Johnson.[9] Addition of 1 to a solution of 6 in tetrahydrofuran at -20°C yielded both regioisomers of 7 (57% yield). These could be converted slowly (24 h) to 8 with DDQ in benzene at 50-60°C in 21% yield. Treatment of 8 with potassium t-butoxide in tetrahydrofuran at -60°C to -30°C yielded nearly pure 3 in 89% yield after chromatography on florisil (pentane).

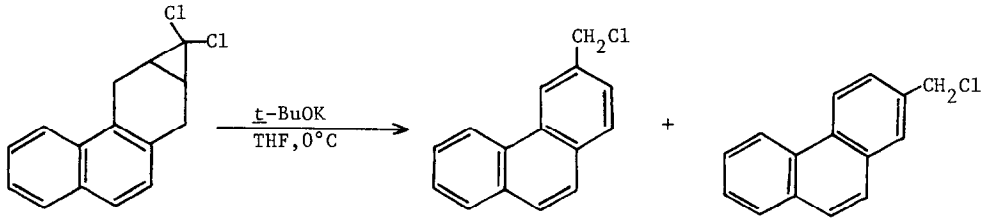
The ^{1}H NMR spectrum of 3 (Figure 1) displays the expected pattern with signals at δ 3.59 (s, 2 H), 7.70-7.96 (m, 6 H), 8.52 (d, 1 H, J = ~ 2 Hz), and 8.70-8.84 (m, 1 H). The ^{13}C NMR spectrum (22.63 MHz, $CDCl_3$) shows signals at δ 19.4 (C1), 108.4 (C9), 114.3 (C2), and other signals at 123.0, 126.3, 127.7, and 128.6. The quaternary carbons were not observed. Other spectral properties are: UV, $\lambda_{max}^{C_5H_{12}}$ 250 nm (log ε 4.75), 320 (log ε 2.87), 327 (log ε 2.71), 335 (log ε 3.09), 343 (log ε 2.63), and 351 (log ε 3.11); IR, 1660 cm^{-1} ("benzene double bond"); high resolution mass spectrum, calcd for $C_{15}H_{10}$: m/e 190.0783, found m/e 190.0781.

Figure 1



90 MHz ^{1}H NMR Spectrum of 1H-Cyclopropa[b]phenanthrene in $CDCl_3$

A earlier attempt to prepare 3 from 9 via the dehydrochlorination-isomerization route[10-13] afforded none of the desired cyclopropparene. Thus addition of dichlorocarbene to 1,4-dihydrophenanthrene[14] yielded 9, m.p. 120-122°C, in 30% yield. The reaction of 9 with potassium t-butoxide in tetrahydrofuran at 0°C for 1.5 h afforded a mixture of 2- and 3-chloromethyl-



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phenanthrene in 70% yield after chromatography on silica gel (hexane). This observation provides further confirmation that this route cannot be utilized in the synthesis of cyclopropanes larger than the cyclopropanaphthalenes.

We are currently pursuing studies which should lead to the remaining three cyclopropaphenanthrenes. Results of these studies will be reported later.

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References

1. National Science Foundation Predoctoral Fellow, 1983-1986.
2. Gulf Oil Foundation Fellow.
3. R. Breslow, G. Ryan, and J. T. Groves, J. Am. Chem. Soc., 92, 988 (1970). These workers report that the dichlorocyclopropenes are explosive and possibly toxic.
4. See also: W. E. Billups, E. W. Casserly, and B. E. Arney, Jr., J. Am. Chem. Soc., 106, 440 (1984).
5. A. Ottolenghi, M. Fridkin, and Z. Fridkin, Can. J. Chem., 41, 2977 (1963).
6. Chan and Massuda have reported the synthesis of 1-bromo- and 1-chlorocyclopropene by treating 1,1-dibromo-2-(trimethylsilyl)cyclopropane and 1,1-dichloro-2-(trimethylsilyl)cyclopropane, respectively, with CsF in diglyme: T. H. Chan and D. Massuda, Tetrahedron Lett., 39, 3383 (1975).
7. The cyclopropene can be trapped in 80-90% yield with cyclopentadiene. A small amount of 1-bromo-2,2-dichlorocyclopropane accompanies the cyclopropene.
8. D. R. Buckle, N. J. Norman, J. W. Ross, H. Smith, and B. A. Spicer, J. Med. Chem., 16, 1334 (1973).
9. R. O. Angus, Jr., and R. P. Johnson, J. Org. Chem., 48, 273 (1983).
10. D. Davalian and P. J. Garratt, Tetrahedron Lett., 32, 2815 (1976).
11. D. Davalian, P. J. Garratt, W. Koller, and M. M. Mansuri, J. Org. Chem., 45, 4183 (1980).
12. W. E. Billups, Acct. Chem. Res., 11, 245 (1978).
13. B. Halton, Ind. Eng. Chem. Prod. Res. Dev., 19, 349 (1980).
14. A. Buquet, A. Couture, and A. Lablache-Combier, J. Org. Chem., 44, 2300 (1979).

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