Tetrahedron Letters,Vol.23,No.40,pp 4095-4098,1982 0040-4039/82/404095-04$03.00/0
Printed in Great Britain

DIHYDROSILAANTHRACENYLIDENE AND DIHYDROANTHRACENYLIDENE

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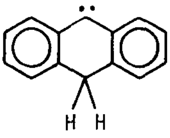
Abstract Carbenes generated from 10-diazo-9,9-dimethyl-9,10-dihydro-9-silaanthracene and 10-diazo-9,9-dimethyl-9,10-dihydroanthracene gave hydrogen abstraction products by the triplet nature of these carbenes. The triplet dihydrosilaanthracenylidene was shown by the electron spin resonance study

The chemistry of arylcarbenes is focused on the problem of spin multiplicity and different reactivities of the singlet and triplet states.[1] Despite various aryl-substituted carbenes have been investigated, dihydroanthracenylidene 1 has so far been missing in a series of carbene species. We have recently prepared 10-diazo-9,9-dimethyl-9,10-dihydro-9-silaanthracene 2a[2] and 10-diazo-9,9-dimethyl-9,10-dihydroanthracene 3a[3], and wish to report here the photolysis of 2a and 3a with a view to examine the spin multiplicity and the reactivity of these new carbenes 2b and 3b.



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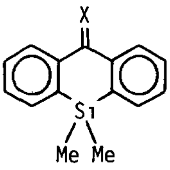
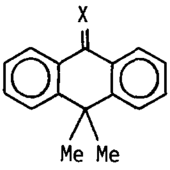
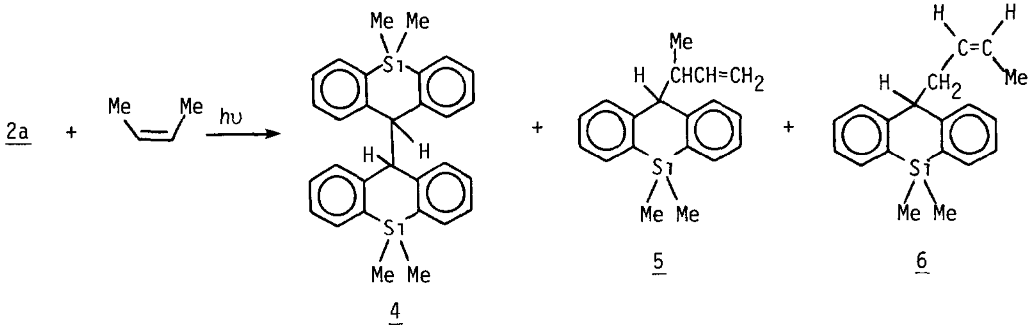


2a, X=N_2
b, X=:

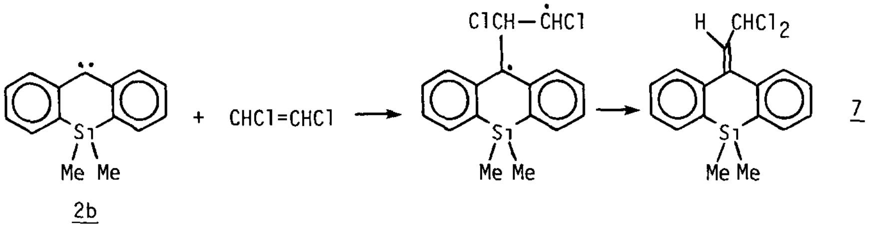


3a, X=N_2
b, X=:
c, X=NNHTs

Irradiation of 2a (260 mg, 1.04 mmol) at 0°C in a mixture of benzene and large excess cis-2-butene with a 400W high pressure mercury lamp resulted in the formation of white precipitates, which was identified as dimer 4 (49%), mp>300°C, NMR($CDCl_3$,δ) 0.57(s,6H,SiMe), 0.83(s,6H,SiMe), 4.05(s,2H,ArCH), and 6.07-7.73(m,16H,ArH); Anal. Calcd for $C_{30}H_{30}Si_2$: C,80.65, H,6.76; Found: C,80.59, H,6.72%. The filtrates contained products 5[4] (22%) and 6[5] (23%) which were separated by preparative gas chromatography. A similar irradiation of 2a in a mixture of trans-2-butene/benzene afforded products 4 (50%) and 5 (21%) in addition to trans isomer of 6[6] (28%). No cyclopropane derivative due to the addition of carbene 2b to cis- and trans-2-butenes was found. The hydrogen abstraction reaction and the lack of addition may be ascribed to the triplet character of carbene 2b.



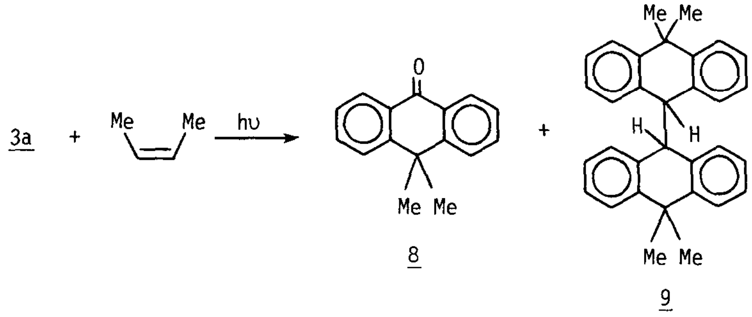
Clear evidence for the triplet carbene 2b was provided when a solution of 2a in trans-1,2-dichloroethylene was irradiated. Product 7 with rearranged chlorine atom was obtained as major product (33%), NMR(CCl_4,δ) 0.48(br.s,6H, $SiMe_2$), 6.25 and 6.53(2H,AB quartet,J=11Hz), and 7.10-7.87(m,8H,ArH).[7]



The triplet nature of the carbene 2b was clearly shown by electron spin resonance study. Thus irradiation of 2a in EPA matrices with a 500W high pressure mercury lamp at ca. 40K in an ESR cavity (with a microwave frequency of 9.173 GHz) gave a set of high field X, Y and Z transition at 4633, 5465, and 7455 G as well as a strong Z transition in the low field (1135 G). The signals are characteristic of triplet carbenes and the resonance field values are analyzed to give zero field splitting parameters as follows, $D = 0.391\ \mathrm{cm}^{-1}$, $E = 0.0215\ \mathrm{cm}^{-1}$. The E value of 2b lies in between those of fluorenylidene ($0.0283\ \mathrm{cm}^{-1}$)[8] and dibenzocycloheptenylidene ($0.0162\ \mathrm{cm}^{-1}$)[9], and the value is larger than that of diphenylmethylene ($0.0194\ \mathrm{cm}^{-1}$).[10] The relatively large E value of 2b indicates that the n type orbital of the carbene 2b has more s character due to the decrease in the angle of the divalent carbon atom.

From the linear Curie-Weiss plots of the intensity of the triplet signals vs. temperature, we are assured of the triplet nature of the ground state 2b. When the temperature of the matrices was raised to ca. 100K, intensity of a doublet signal at 3308 G (g=2.0023) increased at the expense of the triplet signals.

Irradiation of 3a in cis-2-butene produced dimethylanthrone 8 and dimer 9[11] in 8 and 80% yields, respectively. Neither C-H insertion product nor cyclopropane was obtained.



The reactivities of carbenes 2b and 3b are similar to that of dihydrodibenzocycloheptenylidene in which cyclopropane was not formed by the attack of the carbene on cis- and trans-2-butenes.[12] With the foregoing evidence, we conclude that carbenes 2b and 3b are in the triplet state and show the reactivities due to this spin multiplicity.

References and Notes

1. a) W.Kirmse, "Carbene Chemistry", Academic Press Inc. (1971).
   b) M.Jones,Jr. and R.A.Moss, "Carbenes", John Wiley & Sons, Inc. (1973).
2. A.Sekiguchi and W.Ando, Bull. Chem. Soc. Jpn., 1982, 55, 1675.
3. The diazo compound 3a was prepared from hydrazone 3c in 77% yield by the treatment with sodium methoxide in dry pyridine at 70°C, mp 90-91°C (dec.), NMR(CCl_4,δ) 1.65(s,6H,CMe_2) and 6.77-7.62(m,8H,ArH); IR(KBr) 2030 cm^{-1}(N_2).
4. Compound 5: NMR(CCl_4,δ) 0.47(s,3H,SiMe), 0.50(s,3H,SiMe), 0.83(d,J=7Hz, 3H,C-Me), 2.00-2.60(m,1H,C=C-CH), 3.67(d,J=8Hz,1H,ArCH), 4.37-4.90 and 5.23-5.93(m,3H,$CH=CH_2$), and 7.00-7.73(m,8H,ArH); IR(NaCl) 1630 and 905 cm^{-1}($C=CH_2$).
5. Compound 6: NMR(CCl_4,δ) 0.48(br.s,6H,$SiMe_2$), 1.20(d,J=5Hz,3H,C=C-Me), 2.37(t,J=7Hz,2H,$C=C-CH_2$), 3.90(t,J=7Hz,1H,ArCH), 5.07-5.60(m,2H,CH=CH), and 6.93-7.73(m,8H,ArH).
6. Trans isomer of 6: NMR(CCl_4,δ) 0.45(s,3H,SiMe), 0.50(s,3H,SiMe), 1.55(d, J=4Hz,3H,C=C-Me), 2.10-2.50(m,2H,$C=C-CH_2$), 3.97(t,J=7Hz,1H,ArCH), 5.03-5.73 (m,2H,CH=CH), and 7.00-7.83(m,8H,ArH); IR(NaCl) 965 cm^{-1}(CH=CH).
7. Recently, triplet carbenes were shown to give similar products in the reaction with 1,2-dichloroethylene.
   a) J.B.Lambert, K.Kobayashi, and P.H.Mueller, Tetrahedron Lett., 1978, 4253.
   b) M.Jones,Jr., V.J.Tortorelli, P.P.Gaspar, and J.B.Lambert, Tetrahedron Lett., 1978, 4257.
   c) P.P.Gaspar, B.L.Whitsel, M.Jones,Jr., and J.B.Lambert, J. Am. Chem. Soc., 1980, 102, 6108.
8. A.M.Trozzolo, R.W.Murray, and E.Wasserman, J. Am. Chem. Soc., 1962, 84, 4990.
9. I.Moritani, S.Murahashi, M.Nishino, Y.Yamamoto, K.Itoh, and N.Mataga, J. Am. Chem. Soc., 1967, 89, 1259.
10. a) R.W.Murray, A.M.Trozzolo, E.Wasserman, and W.A.Yager, J. Am. Chem. Soc., 1962, 84, 3213.
    b) R.W.Bradon, G.L.Closs, and C.A.Hutchison,Jr., J. Chem. Phys., 1962, 37, 1878.
11. Compound 9· NMR(CCl_4,δ) 1.58(s,6H,CMe), 1.73(s,6H,CMe), 5.60(s,2H,ArCH), and 7.03-7.77(m,16H,ArH).
12. a) I.Moritani, S.Murahashi, K.Yoshinaga, and H.Ashitaka, Bull. Chem. Soc. Jpn., 1967, 40, 1506.
    b) I.Moritani, S.Murahashi, H.Ashitaka, K.Kimura, and H.Tsubomura, J. Am. Chem. Soc., 1968, 90, 5918.

(Received in Japan 15 June 1982)