Tetrahedron Letters,Vol.29,No.47,pp 6141-6142,1988 0040-4039/88 $3.00 + .00
Printed in Great Britain Pergamon Press plc

ISOLATION AND ALCOHOLYSIS OF AN IPSO ADDUCT, VINYLIDENECYCLOHEXADIENE, FROM PHOTOLYSIS OF 1-(p-ETHOXYPHENYL)VINYL BROMIDE

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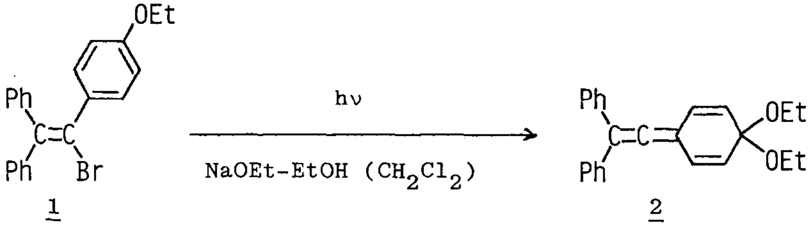
Summary: An ipso adduct, vinylidenecyclohexadiene 2, was isolated from the title photolysis and showed exclusive transformation to the corresponding vinyl ethers by alcoholysis.

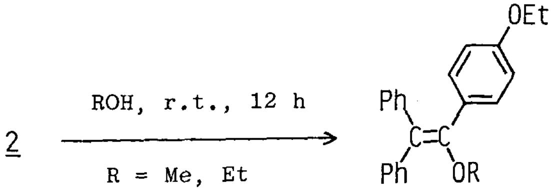
As nucleophilic substitutions of vinyl cations have been well discussed,1) they occur only at the sp carbon of the double bond. However, to the best of our knowledge, ipso ring substitution of arylvinyl cations is unknown. Recently we reported photochemical double cyanation of arylvinyl bromides,2) which mechanism was proposed as the reaction proceeds with ipso substitution on the aryl ring of the vinyl cation followed by nucleophilic displacement. In the receeding paper,3) we described ipso substitution of 1-(p-methoxyphenyl)-2,2-diphenylvinyl bromide by alkoxide anions. Now we wish to report the isolation of the ipso adduct and the behavior toward alcohols to convert the corresponding vinyl ethers.

Irradiation of 1-(p-ethoxyphenyl)-2,2-diphenylvinyl bromide (1) (2 mmol) was carried out in the presence of NaOEt (20 mmol) in EtOH (100 ml)-CH_2Cl_2 (20 ml) under N_2 atmosphere at 0 °C by use of a Pyrex-filtered high-pressure Hg lamp (100 W) for 3 h. After removal of the solvent at 0 °C in vacuo, extraction with ether and the succeeding wash with water afforded 1,1-diethoxy-4-(2',2'-diphenylvinylidene)cyclohexa-2,5-diene (2) in a 88% yield, which crystalized in hexane to give white crystals, mp 96-97 °C.

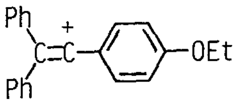


Vinylidenecyclohexadiene 2[4] gives a strong peak due to the molecular ion (M^+) and satisfys with the elemental analysis. The IR shows a characteristic absorption at 1910 cm^{-1} due to the allenic bond. ^1H and ^{13}C spectra are consistent with the proposed structure. Particularly characteristic are the olefinic protons (δ 5.9 and 6.6, J = 10 Hz, AB pattern) in the ^{1}H NMR and the quaternary sp^{3}carbon at δ 95 and the allenic carbon at δ 213 in the ^{13}C NMR.

The noteworthy behavior of 2 is quantitative conversion to 1-(p-ethoxyphenyl)-2,2-diphenylvinyl ether 3. Treatment of 2 with methanol or ethanol (0.01 M, room temperature, 12 h) gave vinyl ether 3 (R = Me or Et)[5] quantitatively. This means that the expulsion of the ethoxyl group from 2 is easy and 2 can serve for regeneration of vinyl cation 4, in analogy with hydrolysis of ketals.[6] The studies concerned with the above subject are now in progress and will be reported in near future.



3 (quant)



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2) T. Kitamura, M. Murakami, S. Kobayashi, and H. Taniguchi, Tetrahedron Lett., 27, 3885 (1986).

3) T. Kitamura, T. Kabashima, S. Kobayashi, and H. Taniguchi, Chem. Lett., submitted for publication.

4) IR (KBr) 3060 (w), 3030 (w), 2980 (s), 2930-2880 (s), 1910 (m, C=C=C), 1650 (m), 1600 (m), 1490 (s), 1440 (s), 1420 (m), 1390 (m), 1200 (s), 1140-1050 (vs), 980 (vs), 900 (m), 770 (s), 750 (m), 700 (vs), 630 (m); ^{1}H NMR ($CDCl_3$) δ 1.21 (t, J = 7 Hz, 6 H, Me), 3.52 (q, J = 7 Hz, 4 H, CH_2), 5.92 (d, J = 10 Hz, 2 H, CH=), 6.56 (d, J = 10 Hz, 2 H, CH=), 7.32 (bs, 10 H, ArH); ^{13}C NMR (C_6D_6) δ 15.94 (CH_3), 57.16 (CH_2), 94.55 (quaternary sp^{3} carbon), 103.34, 111.33, 125.46, 128.57, 128.90, 129.08, 136.06 (sp^{2} carbons), 213.48 ($C{=}\underline{C}{=}C$); MS (EI, m/e) 344 (M^+, 89), 316 (23), 301 (70), 287 (100).

5) 3 (R = Me): mp 124-125 °C; ^{1}H NMR ($CDCl_3$) δ 1.36 (t, J = 7 Hz, Me), 3.40 (s, OMe), 3.92 (q, J = 7 Hz, OCH_2), 6.51-7.18 (m, ArH). 3 (R = Et): mp 88-90 °C; ^{1}H NMR ($CDCl_3$) δ 1.19 (t, J = 7 Hz, Me), 1.36 (t, J = 7 Hz, Me), 3.67 (q, J = 7 Hz, OCH_2), 3.97 (q, J = 7 Hz, OCH_2), 6.60-7.27 (m, ArH).

6) R. G. Bergstrom, in "Supplement E: The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulfur Analogues," ed by S. Patai, John Wiley & Sons, New York (1980), Chap. 20.

(Received in Japan 16 August 1988)