Tetrahedron Letters,Vol.29,No.36,pp 4631-4632,1988 0040-4039/88 $3.00 + .00
Printed in Great Britain Pergamon Press plc

TRANS-ACETOXYMERCURATION OF DIPHENYLACETYLENE

Yu.K.Grishin*, D.V.Bazhenov, Yu.A.Ustynyuk and Nikolai S.Zefirov*
Department of Chemistry, Moscow State University, Moscow 119899, USSR

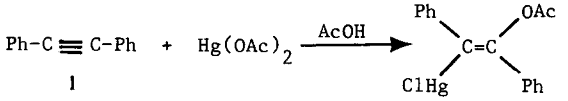
and

V.R.Kartashov*, T.N.Sokolova, E.V.Skorobogatova and A.N.Chernov
Gor'ky Polytechnical Institute, Gor'ky 603600, USSR

Abstract: In contrast with literature data[1,4-6] the acetoxymercuration of diphenylacetylene proceeds to give trans-adduct, 2, the configuration of which was established on the basis of ^{13}C, ^{199}Hg NMR and X-ray data.

Acetoxymercuration of alkylphenylacetylenes [1-3] and dialkylacetylenes [1,4] proceeds predominantly as a trans-addition. However, available data for the parent diphenylacetylene, 1, are still ambiguous [1,4-6]. First, it was reported that oxymercuration of 1 gives both cis- and trans-vinyl mercurials [5]. Later investigations showed the formation of a single isomer with cis-configuration [1,4,6]. Such a different stereochemical result for the oxymercuration of 1 as compared with other 1,2-disubstituted acetylenes seemed unreasonable. Therefore, we decided to reinvestigate the stereochemical course of oxymercuration of 1. The second purpose of the study was to elaborate the NMR criteria for this configurational assignment, as well as to get a deeper insight into the NMR characteristics of unsaturated oxymercurials (cf. [3]).

The oxymercuration of 1 with $Hg(OAc)_2$ [7] yielded the adduct 2 :



1

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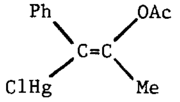

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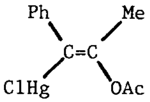

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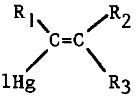
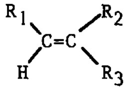
Crystals of 2 are monoclinic, $a=10.648(4)$, $b=10.378(5)$, $c=7.715(7)$ Å , $\gamma=114.95^\circ$, space group $P2_1$, $Z=2$. Cell parameters and intensities of 2118 reflections with $I > 3\sigma(I)$ were collected on CAD-4F diffractometer. The structure was solved by heavy atom methods refined by full-matrix least square, $R=0.040$ [8]. The molecule of 2 is slightly non-planar, with dihedral angle HgC_1C_2O being 178.2°. The main result of this study is the proof of trans-configuration of adduct 2.

We have studied ^{13}C (cf. [9]) and ^{199}Hg NMR spectra of the adduct 2. ^{199}Hg chemical shifts for adducts 2 and 3 [3] are similar (-1155.1 and -1154.2 respectively., ppm relative to Me_2Hg, $CDCl_3$), while compound 4 [3] has a resonance that is shifted markedly upfield (-1191.2 ppm).

TABLE 1. Coupling constants $^2J_{HgC}$ in



and $^2J_{CH}$ in



, Hz.

R_1	R_2	R_3	$^2J_{HgC}$	$^2J_{CH}$
C_6H_5	$OCOCH_3$	C_6H_5	+266.2	+6.9[b]
CH_3	$OCOCH_3$	C_6H_5	+303.9[a]	+8.4[b]
C_6H_5	$OCOCH_3$	CH_3	+301.5[a]	+8.2[b]
C_6H_5	CH_3	$OCOCH_3$	-87.9[a]	-5.4[b]
H	H	H	+27.3[c]	-2.4[d]
H	Cl	H	+319.2[c]	+7.5[e]
H	H	Cl	-115.2[c]	-7.9[e]

[a] Ref.3. [b] Calc. in accordance with Ref. 12.
[c] Ref. 10. [d] Ref. 13. [e] Ref. 14.

It was found previously[3,10] that the value and sign of $^2J_{HgC}$ coupling constants depended on the orientation of the electronegative substituent relative to HgCl. The existence of a correlation of $^2J_{HgC}$ with $^2J_{CH}$ for isostructural series was also noticed[10] (based on the idea of the dominant contribution of the Fermi contact term to spin-spin coupling constants of ^{199}Hg nuclei [11]).

We suggest to use these parameters as a diagnostic tool for the configurational assignment in polysubstituted vinyl mercurials (see $^2J_{HgC}$ in Table 1) Moreover, we calculated $^2J_{CH}$ values for isostructural olefins (Table 1) using additive increments[12]. There exists a good linear correlation (r=0.996) between geminal coupling constants in accordance with eqn (1):

$$\text{eqn (1)} \quad {}^2J_{HgC} = 27.3 \cdot {}^2J_{CH} + 85.2$$

Table 1 shows, that the $^2J_{HgC}$ values and the relationship (1) can be used for configurational assignment of vinyl mercurials even if only a single isomer is available.

REFERENCES AND NOTES

1. S.Uemura, H.Miyoshi and M.Okano, J.Chem.Soc.,Perkin I, 1098 (1980)
2. R.J.Spear and W.A.Jensen, Tetrahedron Letters, 4535 (1977)
3. V.R.Kartashov, T.N.Sokolova, E.V.Skorobogatova, Yu.K.Grishin, D.V.Bazhenov, A.N.Chernov anf N.S.Zefirov, Zh.Org.Khim., in press.
4. R.D.Bach, R.A.Woodard, T.J.Anderson and M.D.Glick, J.Org.Chem.,**47**, 3707 (1982)
5. G.Drefahl, G.Heublein and A.Wintzer, Angew.Chem., **70**, 166 (1958)
6. A.N.Nesmeyanov, A.E.Borisov, I.S.Savel'eva and M.A.Osipova, Izv.Akad.Nauk SSSR, ser.khim 1249 (1961)
7. From 0.89g of **1**, 1.58g of $Hg(OAc)_2$ in 20ml of AcOH and 20 ml of 1% NaCl 2.1g of **2** was obtained (m.p. 139°C).
8. Complete crystallographic data are deposited with the Cambridge Crystallographic Centre.
9. ^{13}C NMR data (100 MHz,$CDCl_3$) and J_{HgC} (Hz): C_1 143.19, 2289, C_2 150.96, 266.2, CO 168.85, 22.0, CH_3 20.78, 9.6, Ph at C_1 - C_i 138.53, 54.3, C_o 128.34, 90.3, C_m 128.73, 15.8, C_p 127.51, 28.1, Ph at C_2 - C_i 137.67, 62.7, C_o 127.05, 13.6, C_m 129.22, C_p 129.85.

10 Yu.K.Grishin D.V.Bazhenov, V.A.Roznjatovsky, M.A.Kazankova, V.R.Kartashov and Yu.A. Ustynyuk, Metallorg.Khim.,**1**, 337 (1988)

11. F.J.Weigert and J.D.Roberts, Inorg.Chem., **12**, 313 (1973)
12. U.Vögeli,D.Herz and W.von Philipsborn, Org.Magn.Res., **13**, 200 (1980)
13. R.M.Linden-Bell and N.Sheppard, Proc.Roy.Soc., Ser A, 269, 385 (1962)
14. K.M.Crecely, R.M.Crecely and J.H.Goldstein, J.Mol.Spectrosc., **37**, 252 (1971)

(Received in UK 11 July 1988)