Tetrahedron Letters,Vol.26,No.16,pp 1967-1968,1985
Printed in Great Britain
0040-4039/85 $3.00 + .00

PHENYL SHIFTS TO VINYL CATIONS FORMED BY IODINATION OF ALKYNES

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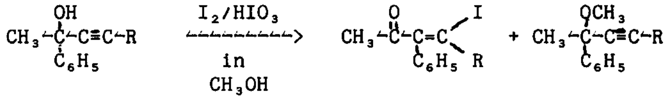
Abstract

Iodine and several of its oxides react with alkynyl alcohols in methanol to afford β-iodo-α,β-unsaturated ketones.

We have observed phenyl shifts to vinyl cations during the reaction of iodine and its oxides with tertiary alkynyl alcohols. Such phenyl shifts have not been reported amidst the extensive literature on vinyl cations generated solvolytically or otherwise.[1,2] A phenyl interaction with a vinyl cation was demonstrated in the bromination of 3-arylpropynes but there was no phenyl shift.[3] Vinyl cationic intermediates have been implicated in the reactions of alkynes and iodine and such oxides as iodine pentoxide, iodic acid, periodic acid or mercuric oxide.[4,5,6]



$$CH_3-C(OH)(C_6H_5)-C\equiv C-R \xrightarrow[\text{in } CH_3OH]{I_2/HIO_3} CH_3-C(=O)-C(C_6H_5)=C(I)R + CH_3-C(OCH_3)(C_6H_5)-C\equiv C-R$$

1 2 3

R = a, C_6H_5; b, H; c, I.

When 2,4-diphenyl-3-butyn-2-ol (1a) in methanol was stirred at room temperature overnight with equimolar amounts of iodine and periodic acid or iodic acid, ketone 2a and ether 3a were the principal products. Dry column chromatography on silica gel with 2% ethyl ether in hexane as eluant or trituration with methanol of the reaction residues freed from iodine afforded 2a in yields of 40-60%: mp 91-92°C; ^1H NMR (CCl_4) 2.45 (s, 3H), 7.2 (m, 10H); ^{13}C NMR ($CDCl_3$) 30.2, 95.8, 127.8, 129.2, 129.4, 129.9, 133.3, 134.1, 139.7, 148.1, 193.6; IR (CCl_4) 1685, 1610 cm^{-1}; MS m/e (rel. int.) 348 (100, M^+), 221 (80, M^+-I), 178 (90, $C_6H_5-C\equiv C-C_6H_5{}^+$); Anal. CHI.[7]

The methyl ether 3a is an artifact of acidic conditions as shown by its quantitative formation by stirring 1a in methanol overnight with periodic acid. If iodine is added to such a mixture and the whole set to reflux, the product of a phenyl-shift, 2a, is the principal product.

The related alcohol, 2-phenyl-3-butyn-2-ol (1b), required the more vigorous conditions of

I_2/I_2O_5 in refluxing methanol to obtain a mixture of the methyl ether 3b and the shifted-phenyl ketone 2b (60%). Both compounds were oils (2b, bp 85°C/5-8 torr; 3b, bp 39°C/0.7 torr). The ketone 2b had ^{1}H NMR absorptions at 2.28 (s, 3H), 6.64 (s, 1H) and 7.22 (s, 5H) in CCl_4. It is considered to be the Z-isomer because treatment of it in refluxing chloroform with a catalytic amount of iodine converted it into the known E-isomer: ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3H), 7.23 (m, 5H), 7.80 (s, 1H).[8] Thus this shift is stereospecific with phenyl migration anti to a possible iodonium-like bridge.

When 1c was treated with I_2/I_2O_5 in refluxing methanol, ketone 2c was formed in about 75% yield: mp 95-96°C; ^{1}H NMR (CCl_4) δ 2.20 (s, 3H), 7.27 (s, 5H); IR (neat) 1700 cm^{-1}; MS m/e (rel. int.) 398 (100, M^+), 271 (50, M^+-I), 228 (70, $C_6H_5C{=}C{-}I^+$); Anal. CHI. It was further noted that ketone 2c was a side-product in the formation of 2b from 1b, presumably by proton loss from the latter's initial iodo-vinyl cation.

Acknowledgments

The authors thank Dr. Robert T. Buckler of the Ames Division of Miles Laboratories for providing helpful spectra. The work was supported in part by a generous grant from the New York University Research Challenge Fund.

References

1. Stang, P.J.; Rappaport, Z.; Hanack, M.; Subramanian, L.R. "Vinyl Cations", Academic Press, New York, 1979.
2. Shchegolev, A.A.; Kanischev, M.I. Russ. Chem. Rev. 1981, 50, 553.
3. Pincock, J.A.; Somawardhana, C. Can. J. Chem. 1978, 56, 1164.
4. Gebeyehu, G.; McNelis, E. J. Org. Chem. 1980, 45, 4280.
5. Cohen, M.J.; McNelis, E. J. Org. Chem. 1984, 49, 515.
6. Janas, J.J.; Asirvatham, E.T.; McNelis, E. Oxid. Commun. 1985 in press.
7. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratories, Woodside, New York. Anal. 2a Calcd. for $C_{16}H_{13}IO$: C, 55.19; H, 3.76; I, 36.45. Found: C, 55.08; H, 3.82; I, 36.21. Anal. 2c Calcd. for $C_{10}H_8I_2O$: C, 30.16; H, 2.01; I, 63.79. Found: C, 30.39; H, 2.01; I, 63.51. Anal. 3a Calcd. for $C_{17}H_{16}O$: C, 86.44; H, 6.82. Found: C, 86.55; H, 6.99. Anal. 3c Calcd. for $C_{11}H_{11}IO$: C, 46.18; H, 3.88; I, 44.35. Found: C, 46.01; H, 5.74; I, 44.24.
8. Spectra of authentic (E)-4-iodo-3-phenyl-3-buten-2-one were provided by Dr. Robert T. Buckler of Miles Laboratories who had reported the preparation of this compound in U.S. 4,238,623 (Dec. 9, 1980).

(Received in USA 18 October 1984)