

Synthesis and Properties of Two α -Phenylazostilbenes. A New Method for the Elimination of Water and *p*-Toluenesulphonate Ion from Substituted Phenylhydrazones¹⁾

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The synthesis of a linear azoalkene, α -phenylazostilbene (**1**), not conjugated to strong electron withdrawing groups is reported. α -(*p*-Methoxyphenylazo)stilbene (**3**) was prepared by a direct method. The mass spectra of **1** and **3** showed a rearrangement yielding positive ions of benzonitrile and benzaldehyde anils (**7**).

We wish to report a facile one step preparation of α -phenylazostilbene (**1**) which appears to be the first²⁾ azoalkene isolated in which the carbon-carbon double bond is not part of a ring³⁾ or conjugated to a strongly electron withdrawing group.⁴⁾ When benzoin phenylhydrazone (α - or β -form, **2**) was stirred with an equimolecular amount of *p*-tosyl chloride in pyridine at 40°C during 10–20 hr, a 45–73% yield of **1** could be obtained as a red stable crystalline solid, mp 90.5–91°C, IR (KBr) bands at 6.94, 10.96, 13.09, 13.22, 13.29, 14.25, and 14.66 μ , PMR (CDCl₃) peaks at 7.16 and 7.34 (m, 14 H) and 7.78 ppm (m, 2 H, δ values). The mass spectrometrically determined MW was 284 (calcd 284) with structurally important ions at *m/e* values of 207 (–Ph), 193 (–PhN), 180 (–H, –C₆H₅CN), 179 (base peak, –PhN₂), 105 (–Ph₂C₂H), 103 (PhCN⁺), 93 (PhN⁺), and 77 (Ph⁺). The structure of **1** was proved chemically by transforming it into benzoin osazone (mp 234–235°C, no depression with authentic sample) upon reflux with phenylhydrazine in glacial acetic acid. The UV spectrum of **1** resembles very closely that of *trans*-azobenzene⁵⁾ with maxima (in *n*-C₆H₁₄)⁶⁾ at 233.0 ($\epsilon=1.38 \times 10^4$), 325.0 (3.54×10^4), 344.5 (3.68×10^4), and 444.0 nm (6.20×10^2). **1** dissolved in 97% sulphuric acid to give a

colourless solution (UV max at 247.0 ($\epsilon=1.135 \times 10^4$), 275.0 (1.042×10^4) and 348.0 nm (1.201×10^4)) which turned violet in *ca.* 10 min (*vis* max at 538.0 nm ($\epsilon=6.97 \times 10^2$)). The stable colouration can be ascribed to the formation of a carbonium ion.⁷⁾ **1** could be exactly titrated with *n*-butyllithium, one equivalent of this reagent being used up for the disappearance of the red colour from an hexane solution of **1**.

The mechanism of formation of **1** appears to involve the *O*-tosyl derivative of **2** for which pyridine performs a 1,4 ionic elimination of *p*-toluenesulphonic acid. Pure pyridine (14 hr at 45°C) produced no **1**.

It is of interest that a derivative of **1**, namely α -(*p*-methoxyphenylazo)stilbene (**3**), was obtained by simply bringing *p*-methoxy-phenylhydrazine in contact with benzoin at 105°C during 14 hr without solvent. The new compound, obtained in 30% yield, was an orange, stable crystalline solid, mp 106–107°C (109–111°C for an analytical sample), whose analysis, MW (M⁺ at 314), infrared, PMR and mass spectra are in agreement with the proposed formula.

The present synthesis affords an easy access to these new compounds which cannot be prepared by the diazo coupling method,^{8,9)} and represent new examples

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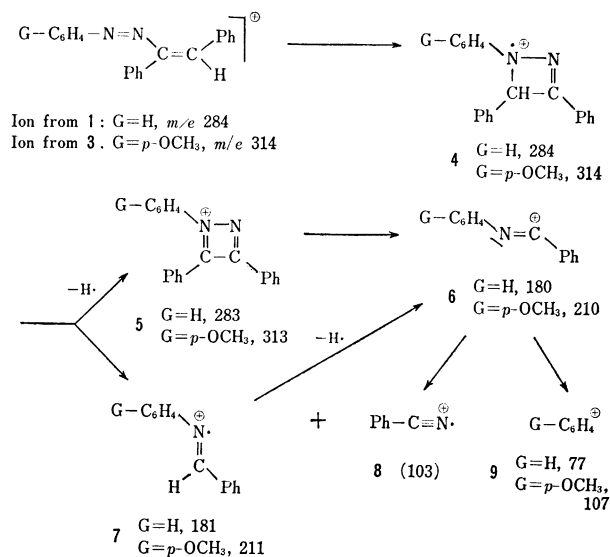
2) During the writing of this manuscript, a paper describing the preparation of **1** from α -chlorodesoxybenzoin and phenylhydrazine appeared: S. Brodka and H. Simon, *Chem. Ber.*, **102**, 3647 (1969).

3) L. Caglioti, P. Grasselli, and G. Rosini, *Tetrahedron Lett.*, **1965**, 4545 and unpublished results from L. Caglioti and G. Rosini; G. J. F. Chittenden and R. D. Guthrie, *J. Chem. Soc., C*, **1967**, 1703 and J. Buckingham and R. D. Guthrie, *ibid.*, **1967**, 1700. See also Ref. 2.

4) J. Van Alphen, *Rec. Trav. Chim. Pays-Bas*, **64**, 109, 305 (1945).

5) H. H. Jaffe, S.-J. Yeh, and R. W. Gardner, *J. Mol. Spectrosc.*, **2**, 120 (1958).

6) The whole spectrum undergoes a red shift of small entity in methanol except for the longest wavelength band. The individual shifts amount to 2.9, 2.9, and 1.4 kcal/mol in the order of increasing wavelength. This can be interpreted in terms of small alteration of charge distribution in the corresponding excited states. Even the longest wavelength maximum, a $n\text{-}\pi^*$ transition is completely unaffected by solvent change, thus indicating that a large charge reorganization should take place. A similar phenomenon was observed for azobenzene: H. H. Jaffe and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, New York (1965), p. 286.



Scheme 1

7) R. Wizinger and B. Cyriax, *Helv. Chim. Acta*, **28**, 1018 (1945).

8) A. P. Terentiev and L. L. Gomborg, *J. Gen. Chem. U.S.S.R.*, **8**, 662 (1938).

9) S. M. Parmenter, Ch. 1 in "Organic Reactions," ed. by R. Adams, J. Wiley and Sons, New York (1959).

of 1,4 sulphonic acid and water¹⁰) elimination in the azoalkene preparation from hydrazonic substrates.

If our interpretation of the low resolution mass spectra of **1** and **3** concerning ions at 180 and 211, respectively, is correct, an interesting rearrangement with intermediate four member ring charged species **4** and **6** took place, as evidenced by the detection of the corresponding fragments **5**, **6**, and **7** (Scheme 1). Structure **5** is very likely to be correct. However, formula **6** most probably only reflects the composition of the actual ion.

Experimental

UV spectra were recorded with a Unicam sp. 800, IR spectra with a Beckman IR 5 (KBr pellet technique), PMR spectra¹¹ with a Varian DP60 and low resolution mass spectra¹¹ with a Perkin Elmer 270. Values of m/e for the 10 highest peaks are reported with relative abundance in brackets. "Half" masses (hm) due to double charged ions and metastable ions (mi) are reported when considered of interest.

α -Benzoin Phenylhydrazone. This compound was prepared according to Smith and Ranson.¹² The solvent was evaporated in a vacuum and the thick residue washed thoroughly with hot hexane. A fractional crystallization from benzene gave the lower melting isomer (β -form, mp 95–96°C): hexane was added to the mother liquor, from which the α -isomer was obtained, mp 159–161°C. Yield: 45% (α and β). One recrystallization from hexane-ether gave slightly yellow compound, mp 161°C (lit.¹²) 158–159°C). PMR (d_6 -acetone): 5.88 (1H, s, CH), 6.31 (1H, s, OH), 6.83 (1H, s, NH), 7.1, 7.2, 7.8 (3H_{ar}, 10H_{ar}, 2H_{ar}, m). UV (hexane) max:¹³ 214.0 ($\epsilon=1.71 \times 10^4$), 235.0 (1.53×10^4), 297.5 (0.79×10^4), and 342 nm (1.97×10^4).

β -Benzoin Phenylhydrazone. This compound was prepared in 57% yield by bringing equimolecular amounts of benzoin and phenylhydrazine¹⁴ in contact at 120°C for 30 min, extracting the resulting thick oil many times with hexane and recrystallizing from hot ethanol, mp 101–102°C (lit.^{12,14}) 106°C). PMR (d_6 -acetone): 4.98 (1H, d, $J=4.5$ Hz, CH), 5.59 (1H, d, $J=4.5$ Hz, OH), 7.25 (15H, m, arom. protons), and 8.15 (1H, s, NH). UV (hexane) max:¹³ 216.0 ($\epsilon=1.71 \times 10^4$), 253.0 (1.39×10^4), 258.0 (1.54×10^4), 264.5 (1.50×10^4), 272.3 (1.48×10^4), and 305.3 nm (1.11×10^4).

The actual structure of the two benzoin phenylhydrazones was discussed by a number of workers.^{13,15,16}

α -Phenylazostilbene (1**).** 1) A solution of 15.09 g *p*-tosyl chloride and 23.94 g of a mixture of α - and β -isomers of benzoin phenylhydrazone in 150 ml dry pyridine was refluxed for 7 hr. An intensely red colouration appeared immediately

and a white precipitate formed. The cool mixture was washed with brine, dried over sodium sulphate and the solvent evaporated to give a red oil. Since direct crystallization from common solvents failed to yield a solid product, absorption chromatography (silica gel, hexane-benzene 1:1 vol) was employed to give 3 well separated fractions: the first eluted was a trace of a rose oil not further analyzed, the second was a red oil (55% yield), which was recrystallized to the desired compound (mp 89–90°C) from methanol, the third unreacted α -benzoin phenylhydrazone (mp 155–158°C).

2) **From Benzoin Phenylhydrazone:** A solution of the α -benzoin phenylhydrazone (3.83 g) and tosyl chloride (3.38 g) in 23 ml pyridine was stirred at 40°C for 33 hr. The red colour appeared very soon after mixing the reactants. The reaction mixture was heated with 50 ml water and extracted with hexane. The organic layer, dried over sodium sulphate, was freed from solvent, to yield a viscous red oil. Chromatography on a 4 $\times$ 30 cm silica gel column, using benzene as an eluent, gave, after a 200 ml forerun, compound **1** (3.60 g, 72.5%, 250 ml) as a thick red oil, homogeneous by tlc analysis (R_f 0.75, on silica gel with cyclohexane-ethylacetate 85/15 vol).¹⁷ Two recrystallizations from alcohol gave red-orange crystals, mp 90.5–91°C (lit.¹) 90°C).

3) **From β -Benzoin Phenylhydrazone:** Using the same procedure as described above for the reaction of the α -form, we obtained the same product **1** 45%, mp 90°C (lit.¹) 90°C), mixed mp with that obtained from the α -form showed no depression.

Found: C, 84.21; H, 5.55; N, 10.04%. Calcd for C₂₀H₁₆N₂: C, 84.47; H, 5.67; N, 9.85%. PMR (CDCl₃):¹⁸ 7.16 and 7.34 (14H, partially overlapped multiplets), 7.78 (2H, m). IR (KBr):¹⁹ 6.26 w, 6.81 w, 6.94 m, 7.02 s, 7.03 m, 7.10 m, 7.41 w, 7.43 w, 7.80 w, 8.66 w, 9.31 w, 9.45 m, 9.49 m, 9.85 m, 9.93 w, 10.95, and 10.98 (doublet, m), 11.32 w, 11.45 w, 12.93 w, 13.09 vs, 13.22 s, 13.29 s, 13.34 vs, 13.59 w, 14.17 vs, 14.25 vs, 14.50 vs, 14.66 vs, 14.69 vs, 16.04 s, 16.47 m, 17.15 s, 19.32 w, 19.38 w, 20.06 s, and 20.19 μ s. UV maxima are indicated in the descriptive part. Mass spectrum:²⁰ 179 (100, –PhN₂), 284 (82, parent peak), 178 (73, PhCCPh⁺), 283 (31, –H), 77 (30, Ph⁺), 180 (26, –H, –PhCN), 285 (18, +H), 177 (12), 181 (10, –PhCN), 105 (10, PhN₂⁺), 193 (10, –PhN) and 207 (10, –Ph); hm: 142.5 (M+1²⁺), 142 (M²⁺) and 141.5 (M–1²⁺).

Reactions of **1.** A) **Reaction with *n*-Butyllithium:** The red colour of a hexane solution of **1** changed to pale yellow and a white precipitate appeared upon dropwise addition of one equivalent of *n*-butyllithium (hexane solution). The reactions were instantaneous. No attempt was made to separate and identify the product(s).

B) **Reaction with Phenylhydrazine:** A mixture of **1** (251 mg) and phenylhydrazine (381 mg) in glacial acetic acid (4 ml) was refluxed for 7 hr, the solvent was then evaporated under reduced pressure, the solid yellow residue taken up with chloroform and washed with aqueous bicarbonate, the organic solution was dried over sodium sulphate and evaporated to yield the crude benzoin osazone, mp 325–328°C.

17) Work in progress in our laboratory by G. Rosini has shown that two stereoisomers of **1** could be obtained from α -acetoxydesoxybenzoin and phenylhydrazine.

18) The physical properties here recorded are identical for **1** from any of the **3** preparations described.

19) This spectrum was recorded with a Perkin Elmer Grating Spectrometer model 225.

20) The sample was vapourized in a chamber of ion source at 85°C; the chamber was kept at 150°C and the electron energy at 80 eV.

10) H. Simon and W. Moldendauer found that 2-cyclohexanolone phenylhydrazone exchanged the OH substituent with a MeO group in methanol in *acidic* conditions. They proposed the intermediary of 1-phenylazocyclohexene, *Chem. Ber.*, **101**, 2124 (1968).

11) We are indebted to Mrs. A. B. Giumanini for recording the spectra.

12) A. Smith and J. H. Ramson, *J. Amer. Chem. Soc.*, **16**, 108 (1894).

13) C. C. Baly, W. B. Tuck, E. G. Marsden, and M. Gazdar, *J. Chem. Soc.*, **91**, 1573 (1907) reported the higher wavelength part of the electronic spectrum of this compound.

14) G. J. Bloink and K. H. Pausaker, *ibid.*, **1952**, 661.

15) S. B. Hendricks, O. R. Wulf, G. E. Hilbert, and U. Liddel, *J. Amer. Chem. Soc.*, **58**, 1991 (1936).

16) E. M. Tanner, *Spectrochim. Acta*, **16**, 20 (1959).

Crystallization from chloroform-ethanol gave a product (43.5%) melting at 234–235°C, showing no depression with an authentic sample of the β -osazone prepared from benzoin and phenylhydrazine in refluxing acetic acid.²¹⁾ Mass spectrum:²²⁾ 386 ($-4H^+$), 298 ($-\text{PhNH}$), 215, 194, 192, 104, 103, 93, 92, 91, 77, and 65.

p-Methoxyphenylazostilbene (**3**). *p*-Anisylhydrazine (5.0 g), prepared according to Padoa's method²³⁾ and benzoin (7.32 g) were heated without solvent at 105°C under reduced pressure (10 Torr) for 1 hr. The reaction of water elimination was very prompt as was the appearance of a red coloration of the melt. The obtained oil was chromato-

graphed in small lots (*ca.* 4 g) on a silica gel 5×40 cm column using benzene as eluent. A 30% yield of a red oil, crystallizing in beautiful red needles from ethanol, mp 110–111.5°C, one spot on tlc, was obtained. Found: C, 80.62; H, 5.57; N, 8.78%. Calcd for $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}$: C, 80.23; H, 5.72; N, 8.91%. PMR (CDCl_3): 15 protons in the "aromatic" region, accounting for all *ar*-H and the olefinic H, with prominent peaks at 6.84, 7.00, 7.17, 7.35, 7.70, 7.85, and a singlet (3H, CH_3) at 3.81. Mass spectrum:²⁰⁾ 314 (100, parent peak), 107 (81, An^+), 179 (64, $-\text{AnN}_2$), 178 (63, PhCCPh^+), 135 (42, AnN_2^+), 77 (34, Ph^+), 211 (20, $-\text{PhCN}$), 315 (19, $+\text{H}$), 313 (17, $-\text{H}$), and 196 (16); *hm*: 157.5 ($\text{M}+1^{2+}$), 157 (M^{2+}) and 149.5 (299^{2+} , $-\text{CH}_3$); *mi*: *ca.* 312 and 85. IR (KBr): 6.25 s, 6.32 m, 6.68 m, 6.95 m, 7.60 w, 7.98 s, 8.47 w, 8.55 w, 8.77 s, 9.73 s, 10.87 w, 11.38 w, 11.92 s, 12.46 w, 13.06 w, 13.16 w, 13.60 m, 14.17 s, 14.51 s, and 15.73 μ w.

21) A. Purgotti, *Gazz. Chim. Ital.*, **22**, II, 611 (1892).

22) The sample was vaporized at *ca.* 160°C, the ion source temperature was kept at 180°C and the electron energy at 70 eV.

23) M. Padoa, *Gazz. Chim. Ital.*, **44**, II, 535 (1914).