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Reactions of 3-Bromocamphor with Phenylhydrazine[1]

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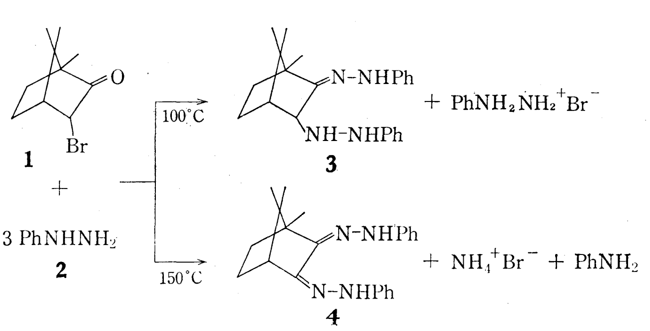
The interaction of 3-bromocamphor (**1**) with phenylhydrazine (**2**) at 100 °C yielded camphor phenylhydrazinophenylhydrazone,[3] perhaps in the tautomeric formula **3**, a colorless crystalline compound, mp 136—137 °C, moderately stable in air, surprisingly[4] stable to prolonged heating at 100 °C *in vacuo* and treatment with **2** at 150 °C. Compound **3** was identified on the basis of its molecular weight (M^+ *m/e* 348), elemental analysis and unequivocal spectral evidences.

When the reaction was carried out at 150 °C, after a few minutes a vigorous exotherm set in with the evolution of ammonia and the formation of aniline to give an excellent yield of camphor osazone **4**, a yellow crystalline compound, mp 149—152 °C, whose structure was supported by spectral characteristics. That the camphor framework was intact was ascertained by the PMR spectrum, which exibited three singlets in 1 : 1 : 1 ratio at δ 0.74, 0.87, and 1.03 ppm, an A_2B_2 quartet centered at 1.48 ppm and a deformed doublet at 2.80 ppm in addition to a complex aromatic pattern. The infrared spectrum of **4** showed two absorption bands for the γ_{NH} at *ca.* 3300 cm^{-1} due to the free and associated secondary amine[5] and the presence of monosubstituted phenyl groups with three bands between 650 and 800 cm^{-1}. The parent peak (M^+ *m/e* 346) was also the most prominent in the mass spectrum at 70 eV. The ultraviolet spectrum was closely similar in band location and relative intensities to that of cyclohexane osazone.[6]



Reciprocal support for structures **3** and **4** was given by the facile conversion of the former into the latter by reflux with **2** in acetic acid.

In an experiment under the conditions and the workup procedure described by Balbiano[3] we isolated only a compound **5** melting at 191—192 °C in a trace

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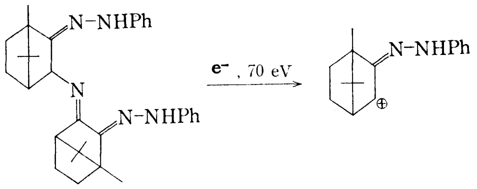
3) A supposed camphor phenylhydrazinophenylhydrazone was described by Balbiano, *Gazz. Chim. Ital.*, **15**, 246 (1886) and **17**, 95 (1887), as a red compound, mp 55 °C.

4) Phenylhydrazinophenylhydrazones are a very rare type of compounds, only two of them having been described: L. Caglioti, G. Rosini and F. Rossi, *J. Amer. Chem. Soc.*, **88**, 3865 (1965); H. Simon, G. Heubach, and H. Wacker, *Chem. Ber.*, **100**, 3106 (1967). These compounds are believed to be the key intermediates on the way to osazones in Weygand's mechanism of osazone formation: for a recent review see: S. Kitaoka, *Kagaku-no-Ryoiki*, **18**, 475 (1964).

5) C. N. R. Rao, "Chemical Application of Infrared Spectroscopy," Academic Press, New York (1963), p. 245.

6) A. G. Giumanini, unpublished results.

amount. Its analytical data fitted the composition $C_{32}H_{41}N_5$, confirmed by the mass spectrum (M^+ *m/e* 495). Strong insolubility in common NMR solvents prevented recording of the PMR spectrum. Infrared analysis of this bright yellow product showed weak absorptions at 3320 and 3160 cm^{-1}, which can be tentatively ascribed to the ν_{NH} of hydrazone functions, strong bands between 650 and 750 cm^{-1} indicating the presence of monosubstituted phenyl groups. The characteristic bornane doublet was found at 1380 cm^{-1}, as well as intense ν_{CH} absorptions in the expected range. Mass spectral data (M^+ *m/e* 495, "aliphatic" peaks at *m/e* 15, 27, 41, 55 and the peak *m/e* 241, which can be hypothetically pictured as **6** together with the other evidences indicated a structure containing intact camphor moieties and phenyl rings, perhaps **5**.



5 **6**

Our results support the theory according to which a phenylhydrazinophenylhydrazone is an intermediate in the formation of osazones under acid catalysis (HBr or AcOH), though it was not confirmed in which elementary step subsequent to **3** the acid intervened.

Experimental

Mp and bp are uncorrected. UV spectra were recorded with a spectrometer Unicam sp. 800. IR spectra were recorded with a Beckman IR 5, calibrated with polystyrene film. Spectra of solids were recorded by the KBr technique.

PMR spectra were recorded with a Varian DP 60, using TMS as internal standard and a frequency meter Hewlett Packard 241 A to establish peak locations (δ values, ppm). Mass spectra were obtained with a double focusing Perkin Elmer 270, with an ion source temperature of *ca.* 200 °C.

Camphor Phenylhydrazinophenylhydrazone (3). **1** (17 mmol) and **2** (54 mmol) were kept at 100 °C under N_2 for 1 hr. About 10 min after immersion into a warm oil bath, a homogeneous, almost colorless solution was formed from which a white precipitate appeared at once. At the end the whole mixture appeared as a red orange solid mass, from which phenylhydrazinium bromide was obtained by repeated washings with dry ether. The ether solution was extracted with chilled 15% HCl, dried over Na_2SO_4 and evaporated to yield a red oil having the smell of camphor. No osazone **4** was present (tlc). Careful sublimation gave some unreacted **1** (8%), whereas the residue solidified upon cooling, mp 55 °C. Addition of a small amount of methanol to this residue separated a compound, mp 191—192 °C after two crystallizations from methanol, in trace amount, mass spectrum (solid inlet 150 °C): M^+ 495, ten highest peaks 92 (100%), 93 (98), 77 (96), 241 (91), 91 (85), 242 (53), 94 (38), 107 (37), 108 (32) and 255 (32); Found: C, 77.00; H, 8.33; N, 14.05%; Calcd for $C_{32}H_{4.}N_5$: C, 77.53; H, 8.34; N, 14.13%; IR bands at 1600, 1500, 1450, 1380, 1310, 1260, 1195, 1150, 1130, 1095, 1070, 1020, 995, 880, 775, 745, 705 and 685 cm^{-1}. This was compound **5**: the mother liquor after its precipitation gave a 47% yield of product **3**, mp 136—137 °C, after crystallization from hexane–ether, UV (95% EtOH): λ_{mar} (ε): 346 (2427), 280 (32680), and 242 (24100) nm; IR: 3250, 3200, 3160, 3100, 2925, 1600, 1550, 1540, 1500, 1495, 1450, 1390, 1337, 1310, 1270, 1240, 1170, 1150, 1140, 1128, 990, 972, 917, 878, 858, 818, 798, 750, and 695 cm^{-1}; Mass spectrum (solid inlet 75 °C, 10 highest peaks): 93 (100%), 92 (99.5), 94 (25), 77 (87), 107 (37), 108 (36), 105 (29), 255 (80), 241 (20), and 159 (15) with M^+ 348; PMR ($CDCl_3$): 7.05 (m, 10H), 3.62 (s, 3H), 2.60 (s, 1H), 1.86 (s, 1H), 1.54 (d, 4H), 1.085 (s, 3H), and 0.965 (s, 3H) ppm; Found: C, 76.12; H, 8.20; N, 16.18%; Calcd for $C_{22}H_{28}N_4$: C, 75.82; H, 8.10; N, 16.08%. This compound was separated from other runs by absorption chromatography on silica gel using hexane–ether as an eluant. A quantitative transformation of **1** was achieved at 100 °C for 4 hr. Compound **3** was recovered unchanged by heating it alone at 100 °C *in vacuo*, refluxing it in methanol and heating it with phenylhydrazine at 150 °C.

Camphor Osazone (4). *A*) A mixture of 115 mmol of **1** was immersed into an oil bath at 150 °C: dissolution of **1** was promptly followed by a vigorous exothermic reaction. When the reaction subsided, the mixture was kept for 5 min at 150 °C, then cooled to 75 °C and taken up with warm water, cooled to room temperature and extracted with concentrated HCl and ether. The dried ether solution (Na_2SO_4) was evaporated to give 7.38 g of a yellow resinous mixture, which turned green at once upon exposure to air. Absorption chromatography (silica gel/ether–hexane) gave 88.5% crude **4**, mp 149.5—152 °C, after crystallization from methanol, pure yield 86%, UV (95% EtOH): λ_{max} (ε): 375 (16940), 304 (13250), and 254 (16640); IR: 3300, 2900, 1600, 1575, 1500, 1380, 1260, 1210, 1160, 1115, 1075, 1020, 995, 915, 880, 840, 785, 750, 715, and 685 cm^{-1}; PMR ($CDCl_3$): 7.21 (m, 10H), 2.80 (d, 1H, $J=7$ Hz), 1.48 (deformed q, 4H, $J=7$ and 25 ± 2 Hz), 1.03 (s, 3H), 0.875 (s, 3H), and 0.74 (s, 3H) ppm; Mass spectrum (solid inlet 100 °C, 10 highest peaks): 346 (M^+), 254, 212, 210, 93, 92, 91, 77, 238, and 347; Found: C, 76.31; H, 7.77; N, 15.92%; Calcd for $C_{22}H_{26}N_4$: C, 76.26; H, 7.56; N, 16.17%.

B) The osazone **4** was obtained in practically quantitative yield by treating **3** with an excess of **2** and a few drops of AcOH at reflux temperature during 30 min. Direct interaction of **1** with **2** in acetic acid did not give good results.