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A simple synthesis of truxene, a building block for optoelectronics and fullerene fragments

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ABSTRACT

Truxene was efficiently synthesized by reduction of truxenone with excess hydrazine hydrate in diethylene glycol at 180 °C without added base, a variation of the Huang-Minlon Wolff–Kishner reduction. The proposed mechanism highlights hydrazine as a nucleophile and a base, extracting protons from the hydrazone and diazene intermediates.

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Truxene (also known as α-truxene, 10,15-dihydro-5*H*-tribenzo[*a*,*f*,*k*]trindene,tribenzylenebenzene), a $C_{27}H_{18}$ star-shaped polycyclic aromatic hydrocarbon (PAH) with C_3-symmetry, first appeared in the chemical literature in 1889[1,2] (Fig. 1). It was synthesized by the reaction of 4-phenylpropionic acid and phosphorus pentoxide, and directly from 1-indanone and sulfuric acid–water (1:1).[1,2] These reactions of 1-indanone were in essence aldol-condensation cyclotrimerizations. Truxene was later synthesized by cyclotrimerization of 1*H*-indene under harsh conditions.[3] However, the reaction had a major deficiency in that it was not regioselective; truxene was accompanied by its constitutional isomer isotruxene (also known as β-truxene, 14,15-dihydro-9*H*-tribenzo[*a*,*f*,*l*]trindene)[3,4] (Fig. 1). For example, heating 1*H*-indene at 300 °C gave truxene and isotruxene in 9% and 5% yields, respectively.[3] The conversion of 3-phenylpropionic acid into truxene was improved by using polyphosphoric acid. Truxene was obtained in 54% yield. However, it was accompanied (38% yield) by the intermediate 2-(indan-1-yliden)-indan-1-one, the aldol-condensation dimerization product of 1-indanone.[5] Oxidation of truxene[2] gave truxenone (also known as 5*H*-tribenzo[*a*,*f*,*k*]trindene-5,10,15-trione,tribenzoylenebenzene), a $C_{27}H_{12}O_3$ polycyclic aromatic ketone (PAK) with C_{3h} symmetry[6,7] (Fig. 1). The synthesis of truxenone by the acid-catalyzed cyclotrimerization of 1,3-indandione[6,7] afforded truxenone in 90% yield,[7] without any contamination by its constitutional

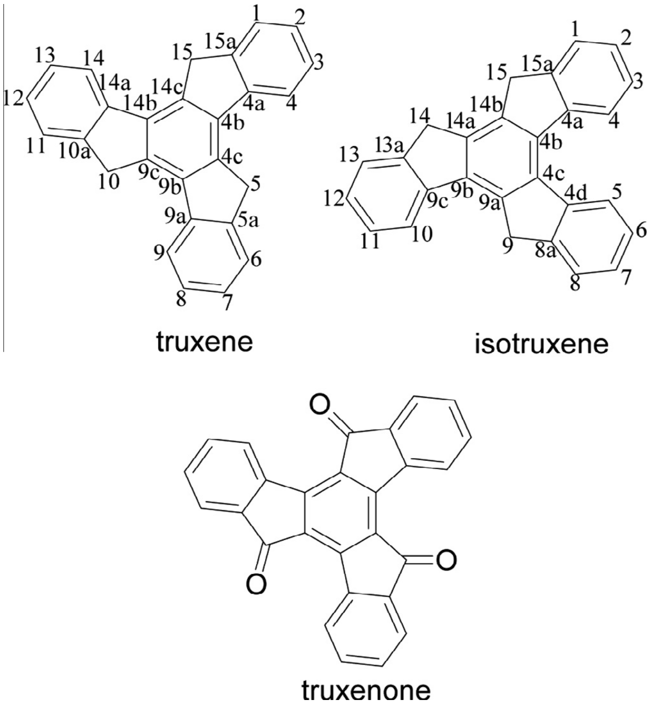

Figure 1. Structures of truxene, isotruxene, and truxenone.

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isomer, isotruxenone (also known as 9*H*-tribenzo[*a*,*f*,*l*]trindene-9,14,15-trione).[8]

Truxene has been recognized as a building block and central core for the construction of materials with promising and diverse applications: larger polyarenes and bowl-shaped fragments of the fullerenes, liquid crystals, C_3 tripod materials in asymmetric catalysis and chiral recognition, candidates for blue light-emitting materials, optoelectronics as active materials in organic field-effect transistors, acceptors in thin-film organic solar cells, liquid crystals and photoresistors, thermally stable cathode buffer materials for organic thin-film solar cells, and water-soluble anionic fluorophores.[9–15]

We report here a straightforward, simple, and efficient synthesis of truxene, uncontaminated with isotruxene, by a variation of the Huang-Minlon modification (also known as Huang Minlon reduction) of the Wolff–Kishner reduction.[16,17] We take advantage of the facile and efficient synthesis of pure truxenone.[6,7] Reduction of truxenone to truxene was affected by hydrazine hydrate in diethylene glycol at 180 °C, without any added base. In addition, we offer a plausible mechanism for a hydrazine-promoted $R^1R^2C{=}O \rightarrow R^1R^2CH_2$ transformation, without promotion by an added base.

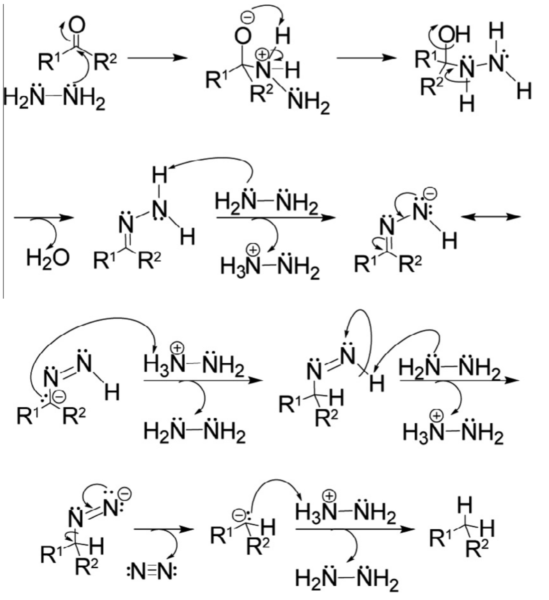
It is generally agreed that the Wolff-Kishner reduction involves the formation of a hydrazone $R^1R^2C{=}N{-}NH_2$ (and H_2O) in a manner analogous to the formation of an imine in the reaction between a carbonyl compound (aldehyde or ketone) and a primary amine.[16] The role of the added base (e.g., OH^-) is to extract two protons, upon heating, first from the NH_2 group of the hydrazone $R^1R^2C{=}N{-}NH_2$ and later from the NH group of the diazene intermediate $R^1R^2CH{-}N{=}NH$.[16,18,19] For the Huang-Minlon modification, the carbonyl compound and hydrazine hydrate, as well as the added base are heated in diethylene glycol, and upon completion of the hydrazone formation, the temperature is raised to 190–200 °C to drive off water and excess hydrazine hydrate.[16] It has been suggested that in the case of fluorenone, a six-fold excess of hydrazine hydrate is required for its conversion into fluorene, and that fluorenone ketazine is presumably formed as an intermediate, which is then reduced to fluorene by hydrazine.[20] A necessary step in these pathways is the departure of the electrofugal leaving group $N{\equiv}N$.

In our hands, truxenone[6,7] reacted with 40 equivalents of hydrazine hydrate (13.3 equiv per carbonyl group) in diethylene glycol at 180 °C for 24 h to give, after a straightforward work-up, truxene in 85% yield. The structure of truxene was verified by its mp, and by ^{1}H NMR and ^{13}C NMR spectroscopy. Complete assignments were made through 2-dimensional correlation spectroscopy (DQF-COSY, HSQC, HMBC, and NOESY). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.29 (^{10}H,^{5}H,^{15}H, s, 6H), 7.40 (^{12}H,^{7}H,^{2}H, dt, J^1 = 7.4 Hz, J^2 = 1.1 Hz, 3H), 7.50 (^{13}H,^{8}H,^{3}H, br t, J = 7.5 Hz, 3H), 7.70 (^{11}H,^{6}H,^{1}H, br d, J = 7.4 Hz, 3H), 7.97 (^{14}H,^{9}H,^{4}H, br d, J = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 36.57 (^{10}C,^{5}C,^{15}C, 3C), 121.87 (^{14}C,^{9}C,^{4}C, 3C), 125.10 (^{11}C,^{6}C,^{1}C, 3C), 126.28 (^{12}C,^{7}C,^{2}C, 3C), 126.92 (^{13}C,^{8}C,^{3}C, 3C), 135.30 (^{9c}C,^{4c}C,^{14c}C, 3C), 137.13 (^{14b}C,^{9b}C,^{4b}C, 3C), 141.71 (^{14a}C,^{9a}C,^{4a}C, 3C), 143.62 (^{10a}C,^{5a}C,^{15a}C, 3C).

When the reaction was carried out with 3.3 and 10 equiv of hydrazine hydrate (1.1 and 3.3 equiv per carbonyl group) at 180 °C for 24 h, the yields of truxene were 17% and 73%, respectively. The unreacted truxenone was identified from its NMR spectra: ^{1}H NMR ($CDCl_3$, 500.2 MHz): δ (ppm) = 7.58 (^{13}H,^{8}H,^{3}H, td, ^1J = 7.4 Hz, ^2J = 0.5 Hz, 3H), 7.74 (^{12}H,^{7}H,^{2}H, td, ^1J = 7.7 Hz, ^2J = 0.7 Hz, 3H), 7.87 (^{14}H,^{9}H,^{4}H, dq, ^1J = 7.4 Hz, ^2J = 1.0, 3H), 9.31 (^{11}H,^{6}H,^{1}H, td, ^1J = 7.7 Hz, ^2J = 0.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125.78 MHz): δ = 123.98 (^{14}C,^{9}C,^{4}C, 3C), 128.70 (^{11}C,^{6}C,^{1}C, 3C), 129.64 (^{14b}C,^{9b}C,^{4b}C, 3C), 131.77 (^{13}C,^{8}C,^{3}C, 3C), 135.50 (^{12}C,^{7}C,^{2}C, 3C), 136.00 (^{14a}C,^{9a}C,^{4a}C, 3C), 141.59 (^{10a}C,^{5a}C,^{15a}C, 3C), 147.72 (^{9c}C,^{4c}C,^{14c}C, 3C), 191.98 (^{10}C,^{5}C,^{15}C, 3C). The ^{1}H NMR spectra also allowed the determination of the truxene:truxenone ratio, based on the 4.29 ppm singlet (truxene) and the 9.31 ppm doublet (truxenone). There were no indications for the formation of truxenone hydrazone, truxenone trihydrazone, truxenone ketazine, truxenone azine, or a truxene dimer (e.g., bitruxenylidene). At 140 °C (40-fold excess of hydrazine hydrate, 65 h), the yield of truxene was only 17%. At 160 °C (24 h), 190 °C (24 h), and 220 °C (30 h) (40-fold excess of hydrazine hydrate), the yields of truxene were 52%, 80%, and 83%, respectively. The attempted reactions of truxenone with hydrazine hydrate in boiling ethanol, 1-butanol, or acetic acid afforded only starting truxenone.

The successful carbonyl to methylene transformation, using hydrazine hydrate in diethylene glycol solution at 180 °C without an added base is presumably due to the ability of hydrazine to act as a base (pK_a = 8.1)[21] toward the acidic hydrogen atoms of the hydrazone and diazene intermediates at the high temperature of the reaction. A proposed mechanism for the variation of the Huang-Minlon modification is presented in Scheme 1. The first equivalent of hydrazine acts as a nucleophile to give the hydrazone. The additional equivalent of hydrazine acts as a base, first extracting a proton from the NH_2 group of the hydrazone $R^1R^2C{=}N{-}NH_2$ to give $R^1R^2C{=}N{-}NH^-$, and later extracts a proton from the intermediate diazene, $R^1R^2CH{-}N{=}NH$. The resulting diazene anion $R^1R^2CH\text{-}N{=}N^-$ is now susceptible to the departure of the electrofugal $N{\equiv}N$ leaving group with the concomitant formation of the carbanion $R^1R^2CH^-$, which is then converted into the methylene product $R^1R^2CH_2$. It is interesting to note that hydrazine does not act as a double-hydride donor in the reduction process, but by formal donation of its nitrogen electron lone pairs. The two hydrogen atoms in the resulting methylene product are donated as protons, not as "hydrides". Only one equivalent plus a catalytic amount of hydrazine are required. According to the proposed mechanism, three equivalents of hydrazine hydrate are needed, whereas 40 equivalents were utilized to obtain the maximum yield. The excess of hydrazine hydrate, bp 114 °C compensates for its loss at the reaction temperature of 180 °C.

Although it has been taken for granted that an alkaline catalyst is necessary to promote the Wolff-Kishner reduction,[17] cases where the reductions have been affected at high temperatures in the absence of a base have been reported, in particular the



Scheme 1. Proposed mechanism of the Huang-Minlon reduction without added base.

reduction of 9*H*-fluoren-9-one to 9*H*-fluorene.[17,20,22,23] An interesting variation of this motif, including the departure of the N≡N leaving group, is the intramolecular reaction of 1,1′-biphenyl-2,2′-dicarboxaldehyde with hydrazine in boiling acetic acid which gave phenanthrene.[24] Likewise, 1,4,5,8-tetrabenzoylnaphthalene underwent a double intramolecular cyclization under the Huang-Minlon modification procedure to give 1,4,7,8-tetraphenylacenaphtho[5,6-*de*][1,2]diazepine. [25]

In conclusion, application of the Huang-Minlon reduction procedure to the reduction of truxenone with excess hydrazine, but without added base, provides a simple and efficient synthesis of pure truxene in excellent yields. A mechanism for the Huang-Minlon reduction is proposed in which hydrazine acts not only as a nucleophile, but also as a base. The application of the Huang-Minlon reduction without added base is expected to be useful for the reduction of aldehydes and ketones, which are sensitive to the added base.

Experimental

Truxenone (1.10 g, 2.86 mmol)[6] in diethylene glycol (100 ml) was added to a round-bottom flask, containing a magnetic stir bar, a dropping funnel and a Y adaptor. The mixture was heated to 180 °C. When all the truxenone has dissolved, a solution of hydrazine hydrate (3.6 ml, 114 mmol) in diethylene glycol (23 ml) was added dropwise with stirring. The original yellow–greenish solution turned gradually brown–yellow. The mixture was stirred at 180 °C for 24 h and then poured into H_2O (500 ml) and stirred overnight. CH_2Cl_2 (100 ml) was then added with stirring. After 6 h, the resulting two liquid phases and solid were separated, first by filtration to give the solid, followed by separation of the organic and aqueous layers. The aqueous fraction was extracted with CH_2Cl_2 (1 × 100 ml) and the combined organic fractions were washed with H_2O (2 × 100 ml) and dried ($MgSO_4$). The CH_2Cl_2 was removed by evaporation under reduced pressure. The resulting crude product (0.821 g) consisted mostly of truxene. The solid contained only truxene (0.020 g). The crude product was triturated with hot acetone to give pure truxene in 85% yield; mp 368–369 °C (dec) [lit., mp 369–370 °C (dec)]. [26]

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