cis-trans-Configuration of α-Azidochalkones

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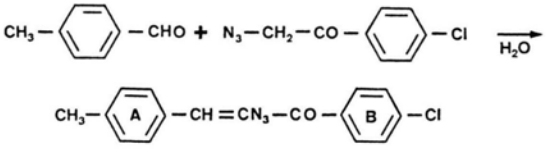
The two stereoisomeric α-azidochalkones (1,3-diaryl-2-azidopropenones) are selectively obtainable, depending on the temperature, by condensation of aldehydes with α-azidocarbonyl compounds. For the higher melting point compound the *trans* configuration is proved by single crystal X-ray analysis of its triphenylphosphazeno derivative.

Analogous isomers may now be characterised from their ^{1}H NMR parameters.

Enazides reported by Smolinsky, Hassner and others [1–5] are suitable precursors to various N-heterocycles [4] and are also mechanistically of interest concerning the formation of unsaturated nitrenes [6]. Moreover, they may be of use in the electrochemical synthesis of enamine and aminocarbonyl compounds [D. Knittel, unpublished]. The preparation of unsaturated azidocarbonyls from aldehydes and α-azidocarbonyls in an one-step reaction has been discussed previously [7–9]. Condensation of *p*-tolylaldehyde with *p*-chloro-α-azidoacetophenone yields selectively either the *trans* or the *cis* form, though the existence of only one – thermodynamically stable – isomer has been postulated [2].



This selectivity can be explained by assuming a more stable intermediate for **1** but a kinetically favoured aldol for **2**. The products formed are only slightly soluble in the solvent used; thus attainment of equilibrium is hindered and the less stable compound is produced.

An assignment of configurations from ^{1}H NMR spectra (see Fig. 1) is difficult because the signal of an olefinic proton is shifted by *ca.* +0.4 ppm by a *cis* CO group but by *ca.* —0.45 ppm by a *trans* N_3 group [3]. Since in electrochemical processes a knowledge of the geometries of substrates is important the structure of **1** was determined *via* an X-ray investigation of the triphenylphosphazeno derivative (**3**).

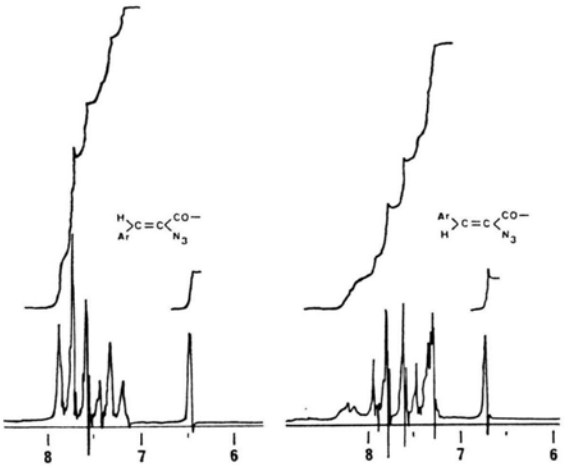
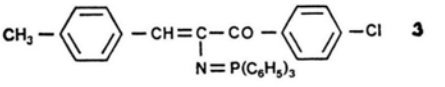


Fig. 1. ^{1}H NMR *vs.* TMS, $CDCl_3$ of **1** (left) and **2** (right).



3

This is formed without changing the conformation of **1** [10] and is more stable in the X-ray beam. As can be seen from Fig. 2, **1** must be assigned the *trans* form, the torsion angle N–C(8)–C(9)–H(9) being 177(1)°. However, the dihedral angle of 56(1)° between the planes of the aromatic nuclei C(1) to C(7) and C(10) to C(16), and the torsion angle O–C(7)–C(8)–C(9) = —151(1)° may differ from the enazide, due to the bulky $P(C_6H_5)_3$ group.

In future it should be possible to determine by NMR spectroscopy the configuration of stereoisomers produced in analogous reactions; the olefinic signals differ by about 0.25 ppm and the signals of the aromatic protons (if present) in ring A are also different (see Fig. 1).

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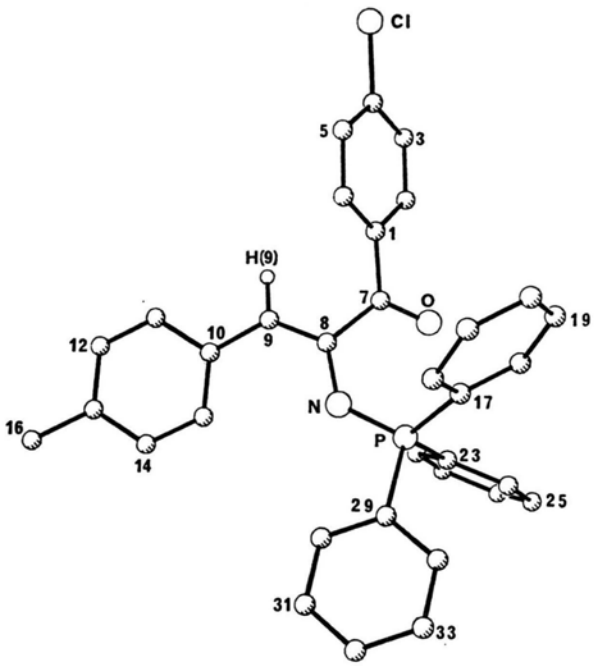

Fig. 2. A perspective view of the structure of **3** and the numbering scheme adopted.

Experimental

1-(p-Chlorophenyl-)-2-azido-3-(p-tolyl-)-2-propene-1-one (**1**): prepared by reaction of *p*-tolylaldehyde with *p*-chloro-ω-azido-acetophenone [8] at 25 °C resulting in an 80% yield of pale yellow crystals of m.p. 100 °C (dec., EtOH).

^{1}H NMR (16% in $CDCl_3$/TMS): δ 2.39 (s; 3 H), 6.46 (s; 1 H), 7.50 (qc; 4 H), 7.70 (qc; 4 H).

cis-Azidochalkone (**2**): the same procedure was followed, except that the reaction temperature was kept below 10 °C. 70% of pure **2** (checked by NMR) were obtained, m.p. 58 °C (petrol ether).

^{1}H NMR (as above): δ 2.23 (s; 3 H), 6.70 (s; 1 H), 7.70 (qc; 4 H), 7.2–7.4 (m; 3 H), 8.22 (m; 1 H).

1-(p-Chlorophenyl-)-2-(triphenylphosphazeno-)-3-(p-tolyl-)-2-propene-1-one (**3**): prepared by refluxing **1** with slight excess of triphenylphosphine. 90% yield of orange crystals, m.p. 149 °C (benzene) were obtained.

^{1}H NMR ($CDCl_3$/TMS): δ 2.30 (s; 3 H), 6.05 (s; 1 H), 6.8–8.2 (m; 23 H). A sample for X-ray analysis was obtained by recrystallisation from benzene.

X-ray Analysis of **3**

Crystal data: $C_{34}H_{27}ClNOP$, M = 532.0, space-group $P2_1/n$, a = 1206.9(6), b = 1494.7(8), c = 1604.7(11) pm, β = 98.89(2)°, Z = 4, d_{calc} = 1.235, d_{exp} = 1.23 Mg m^{-3}. 2973 unique observed ($F > 3\sigma(F)$) diffractometer data, collected between 2θ = 6—46° with monochromated $Mo_{K\alpha}$-radiation and corrected for Lp but not for extinction and absorption effects (μ = 0.211 mm^{-1}), were used for solving the structure by direct methods and for anisotropic refinement by blocked cascade least-squares methods (R = 0.052). For H atoms (in calculated positions) a 'riding model' was employed [11]. Atomic parameters, bond lengths and angles, torsion angles and lists of observed and calculated structure amplitudes may be obtained from G. W. on request.

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[11] All programs used were written by G. M. Sheldrick, Göttingen.