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Note

Gas chromatographic analysis of *trans*- and *cis*-dypnone

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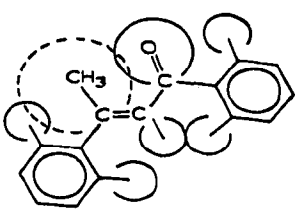
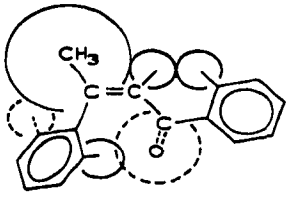
Two geometrical isomers of 1,3-diphenyl-2-buten-1-one (dypnone), *trans*- (I) and *cis*- (II), are known[1]. Their preparation and interconversion, as well as several derivatives of both the *cis*- and the *trans*-isomers, have been reported, the structural analysis being carried out by a UV absorption method.



I



II

In this paper we describe a more accurate separation of the two isomers by preparative gas–liquid (GLC) and thin-layer chromatography (TLC), and the spectroscopic properties of the two pure isomers are discussed.

EXPERIMENTAL

A Cary 14 instrument was used in order to obtain the UV spectra, and a Varian A/56–60 for the NMR spectra. For GLC, a Perkin-Elmer 800 gas chromatograph and a Perkin-Elmer F21 preparative gas chromatograph, both equipped with a flame ionization detector, were used.

Preparation of dypnone

Dypnone was prepared by the method of Wayne and Adkins[2]; the fraction with $b.p._{0.05\ mm}$ 150–158° gave satisfactory analytical results.

Separation of the isomers

GLC indicated that the *trans*- and *cis*-isomers were present in the proportions

89:11 in the distillate. The *trans*-isomer, separated from the mixture by preparative GLC or TLC, gave a UV absorption maximum at 296 nm (ε = 16,320) in ethanol and a shoulder at 265 nm (ε = 10,650). The NMR spectrum in carbon tetrachloride showed two multiplets at 2 and 2.6 τ corresponding to ten aromatic hydrogen atoms, a quartet (1 H), J = 1.2 cps, centred at 2.98 τ corresponding to the olefinic hydrogen atom, and a doublet (3 H), J = 1.2 cps, centred at 7.45 τ corresponding to the methyl hydrogen atoms.

By irradiating a 0.2 M solution of dypnone in *n*-hexane with UV radiation (Quarz Lampen Gas, Hanau, G.F.R.) for 150 h (refs. 1–3), the proportion of the *cis*-isomer in the mixture was increased from 11 to 69% (Figs. 1a and 1b). From this solution, *cis*-dypnone was separated by preparative TLC, and its solution in ethanol gave a UV maximum at 251 nm (ε = 13,188) with shoulders at 240 nm (ε = 11,500) and 280 nm (ε = 11,400). The NMR spectrum in carbon tetrachloride showed two multiplets at 2.2 and 2.8 τ, corresponding to ten aromatic hydrogen atoms, a quartet (1 H), J = 1.2 cps, centred at 3.5 τ due to the olefinic hydrogen atom, and a doublet (3 H), J = 1.2 cps, centred at 7.82 τ due to the methyl hydrogen atoms.

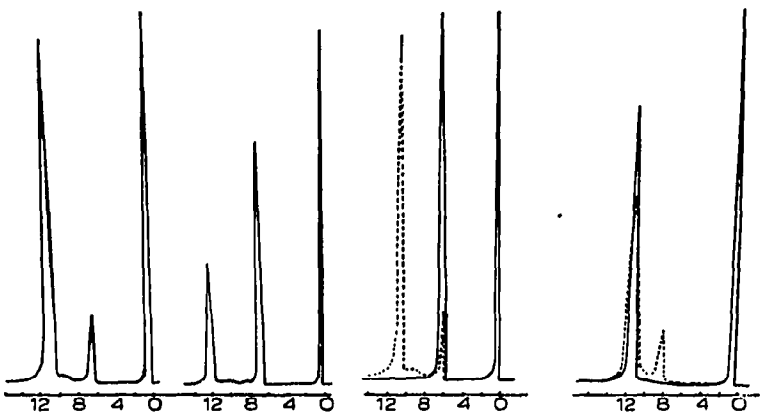


Fig. 1. Gas–liquid chromatograms of dypnone. (a) Mixture of isomers: *trans*-, 89%; *cis*-, 11%. (b) Mixture after irradiation for 150 h: *trans*-, 31%; *cis*-, 69%. (c) – – –, Mixture of isomers; ———, *cis*-dypnone separated by TLC. (d) – – –, Mixture of isomers; ———, *trans*-dypnone separated by TLC.

Thin-layer chromatography

Analytical TLC was carried out with silica gel F_{254} plates of dimensions 20 × 5 cm and thickness 0.25 mm (Merk, Darmstadt, G.F.R.); for development a mixture of toluene and *n*-hexane (2:1) was used. The R_F values were 0.25 for the *trans*-isomer and 0.08 for the *cis*-isomer. Preparative TLC was carried out on silica gel F_{254} plates of dimensions 20 × 20 cm and thickness 2 mm (Merk) with the same developing solution; 0.1 g of the mixture, dissolved in 1.2 ml of diethyl ether, was applied each time. In the zones of interest, the support material was removed and extracted with 125 ml of diethyl ether. The solvent was then removed *in vacuo*.

Gas chromatography

The following columns were used, with nitrogen as carrier gas:

(A) 1.80-m steel column (1/4 in. I.D.) packed with 12% SE-30 on Anakrom 545 A (90–100 mesh);

(B) 2-m steel column (1/8 in. I.D.) packed with 5% silicone oil DC 200 on Chromosorb W AW HMDS (80–100 mesh);

(C) 2-m steel column (1/8 in. I.D.) packed with 5% OV-17 on Anakrom ABS (80–90 mesh).

The retention times (t'_R) are reported in Table I.

The quantitative determination of the two isomers was carried out with a Perkin-Elmer SIP 1 GC data system.

The preparative GC of *trans*-dypnone was carried out with a 1-m steel column (3/4 in. I.D.) packed with 10% OV-17 on Chromosorb A (60–80 mesh); the flow-rate of nitrogen was 350 ml/min, oven temperature 210°, injector temperature 250° and detector temperature 260°.

TABLE I

GAS CHROMATOGRAPHIC CONDITIONS AND RESULTS

Column	*Injector temperature (°C)*	*Oven temperature (°C)*	*N_2 flow-rate (ml/min)*	*t'_R (cis) (min)*	*t'_R (trans) (min)*	*t'_R (trans)/t'_R (cis)*
A	250	250	70	7.5	11	1.42
B	250	180	20	6.8	12	1.7
C	250	185	20	8.4	15.2	1.8

RESULTS

As shown in Table I, the best separation of the isomers was achieved under the conditions indicated for column C. A comparison of the chromatogram of the original mixture with those of the purified isomers (Figs. 1c and 1d) shows that no isomerization occurred in the column. It should be noted that UV analysis cannot reveal the small amount of the *cis*-isomer present in the original distillate, the spectrum of the mixture being coincident with that of the *trans*-isomer.

The assignment of the structure *cis* (II) to the isomer with the lower retention time is based on the UV absorption and NMR spectra, while no conclusive information is obtained from IR or mass spectrometry. The *cis*-isomer has, in fact, a marked deviation from coplanarity of the conjugated system, which causes a decrease in the intensity of the low-frequency UV band analogous to that observed for *cis*-chalcone[1–4], and a deshielding of both olefinic and methyl hydrogen atoms in comparison with the *trans*-isomer.

REFERENCES

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