

Fulvenes and Thermochromic Ethylenes. Part LXVIII.¹ The Stereochemistry of the Wittig–Horner Reaction with Fulvenic and Related Ketones

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The Wittig–Horner reaction with asymmetrically substituted derivatives of 5*H*-dibenzo[*a,d*]cyclohepten-5-one, 10,11-dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5-one, and thioxanthen-9-one has been shown to yield mixtures of two geometrical isomers. The isomers have not been isolated, but their presence has been proven by t.l.c., electric dipole moment measurements, and n.m.r. spectroscopy; the *cis*–*trans* ratios determined by these methods are 1 : 1 in the first and third cases, and 1 : 2 in the second.

THE exocyclic double bond in fulvenes and heptafulvenes is usually not considered a 'normal' double bond because of its dipolar character in the ground state.^{2–4} Nevertheless, the existence of *cis*- and *trans*-isomers with respect to this bond has been established.¹ In some cases [*e.g.* 2-nitro-9-(4-nitrobenzylidene)fluorene⁵ and 2-bromo-9-(4-nitrobenzylidene)fluorene⁶] stereoisomers have been isolated; but, as in these substances the *para*-nitro-group affects the polarity of the exocyclic bond, conclusions drawn from these cases cannot necessarily be generalized.

In the recently reported syntheses⁷ of 3-chloro-5-(4-cyanobenzylidene)-5*H*-dibenzo[*a,d*]cycloheptene (I), 3-chloro-5-(4-cyanobenzylidene)-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene (II), and 2-chloro-9-(4-cyanobenzylidene)thioxanthen (III) by the Wittig–Horner reaction, only one product was isolated; although these

substances could in principle exist as two stereoisomers (*cis* and *trans*), there was no indication that more than one product was obtained. The Wittig–Horner reaction sometimes favours the formation of only one of the two possible geometrical isomers; in the cases under discussion it was therefore not clear whether the Wittig–Horner reaction was stereospecific (yielding either the *cis*- or the *trans*-isomer) or whether the exocyclic 'fulvenic' double bond had so low an energetic barrier to rotation as to make *cis*–*trans* isomerism impossible. However, further investigations have now shown that the Wittig–Horner reaction gives not a single compound, but a mixture of two well defined geometrical isomers. These isomers have not been isolated; their existence and nature have been established by a study of their physical properties.

Thin-layer Chromatography.—T.l.c. on silica gel did not reveal the presence of two isomers in the Wittig–

¹ Part LXVII, I. Agranat, M. Rabinovitz, M. Weissman, and M. R. Pick, *Tetrahedron Letters*, in the press.

² E. D. Bergmann, *Progr. Org. Chem.*, 1955, **3**, 81.

³ E. D. Bergmann, *Chem. Rev.*, 1968, **68**, 41.

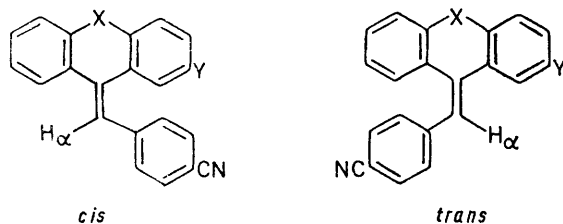
⁴ M. Rabinovitz, I. Agranat, and E. D. Bergmann, *Tetrahedron*, 1966, **22**, 225.

⁵ E. D. Bergmann and E. Fischer, *Bull. Soc. chim. France*, 1950, 1084.

⁶ E. D. Bergmann, E. Fischer, and Y. Hirshberg, *Bull. Soc. chim. France*, 1950, 1103.

⁷ E. D. Bergmann and A. Solomonovici, *Synthesis*, 1970, 183.

Horner reaction products. However, when silica gel impregnated with silver nitrate was used, two spots of similar intensity were easily detected in u.v. light.



- (I) X = CH:CH, Y = Cl
 (II) X = CH₂:CH₂, Y = Cl
 (III) X = S, Y = Cl
 (IV) X = CH:CH, Y = Me
 (V) X = CH₂:CH₂, Y = Me

This established the non-homogeneous nature of the products (I)—(III). The fact that the separation is effected by silver nitrate further suggests that the two species may be geometrical isomers.

three compounds were used for the measurement of intramolecular angles. For the vector calculations the moments of the unchlorinated compounds, 5-(4-cyanobenzylidene)-5*H*-dibenzo[*a,d*]cycloheptene, 5-(4-cyanobenzylidene)-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene, and 9-(4-cyanobenzylidene)thioxanthen (Table 2), were taken as being directed along the C≡N bond (although, because of a small contribution of the polycyclic system to the moment, this is only an approximation). The group moment of C-Cl (taken as 1.58 D) was then added at the angle determined on the model (given in Table 1). This yields for each compound two calculated values of the moment (one for the *cis*- and one for the *trans*-isomer), differing by as much as 1.5 D. Comparison of these calculated moments with the measured values (Table 2) not only confirms that the reaction products are mixtures of isomers, but permits a rough evaluation of the proportion of each isomer present, about 1 : 1 in the cases of the 5*H*-dibenzo[*a,d*]cycloheptene and thioxanthen derivatives (I) and (III) and about 1 : 2 (*cis* to *trans*) in the case of the 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene derivative (II) (Table 1).

TABLE 1

Substance	Isomer	Calculated dipole moments			
		Angle (°) between the moments of the two polar groups	Calculated moment (D)	Experimental moment (D)	Percentage of isomer present
(I)	<i>cis</i>	55	5.26	4.55	51
	<i>trans</i>	120	3.67		49
(II)	<i>cis</i>	67	5.36	4.50	34
	<i>trans</i>	120	3.99		66
(III)	<i>cis</i>	60	5.27	4.14	46
	<i>trans</i>	120	2.85		54

TABLE 2

Experimental data on dipole moments (solutions in benzene; 30 °C)

Substance	α'	β'	P/cm^3	R/cm^3	μ/D
5-(4-Cyanobenzylidene)-5 <i>H</i> -dibenzo[<i>a,d</i>]cycloheptene (I)	25.99	-1.35	459.1	104.6	4.20
	30.12	-1.77	521.7	106.1	4.55
5-(4-Cyanobenzylidene)-10,11-dihydro-5 <i>H</i> -dibenzo[<i>a,d</i>]cycloheptene (II)	29.52	-1.25	514.6	100.9	4.54
	30.42	-0.52	526.2	118.9	4.50
9-(4-Cyanobenzylidene)thioxanthen (III)	23.31	-1.39	420.4	107.1	3.95
	25.78	-1.69	461.7	116.6	4.14

Dipole Moment Measurements.—As each of the compounds (I)—(III) contains two well defined polar groups (CN and Cl) electric dipole measurements were used for the study of their conformation. The dipole moment of each isomer can be calculated by vector addition of known group moments (Table 1). There is some uncertainty with regard to the geometry of the molecules investigated, which are known to be non-planar.^{8,9} A previous study of the conformation of 5*H*-dibenzo[*a,d*]cyclohepten-5-one and of 10,11-dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5-one⁸ has shown the Dreiding models to represent such molecules accurately. The same procedure was applied here, and Dreiding models of the

Nuclear Magnetic Resonance Study.—The presence of the two geometrical isomers was unequivocally proven by a detailed n.m.r. study. Comparison of the spectra of 9-(4-cyanobenzylidene)thioxanthen and of its 2-chloro-derivative (III) showed only one α -proton absorption (at 6.85 p.p.m.) for the parent compound, but two distinct signals (6.81 and 6.85 p.p.m.) for the chlorinated one; these were assigned to the two isomeric forms in 1 : 1 ratio. However, no similar double signals were observed in the spectra of 3-chloro-5-(4-cyanobenzylidene)-5*H*-dibenzo[*a,d*]cycloheptene (I) and its 10,11-dihydro-analogue (II). This fact was attributed to insufficient nonequivalence of the α -protons in the two isomers. In

⁸ H. Weiler-Feilchenfeld and A. Solomonovici, *J. Chem. Soc. (B)*, 1971, 869.

⁹ H. Shimanouchi, T. Hata, and Y. Sasada, *Tetrahedron Letters*, 1968, 3573.

order to increase the sensitivity of the method the corresponding 3-methyl derivatives, (IV) and (V), were prepared. The 3-methyl signal proved to be a sensitive probe for the detection of the two possible stereoisomers.

In the methyl absorption region two clearly distinct signals could be seen, at 2.18 and 2.42 p.p.m. for (IV) and at 2.14 and 2.35 p.p.m. for its 10,11-dihydro-analogue (V). From a comparison with the spectra of the parent ketones, the high-field absorption was assigned to the *cis*- and the low-field one to the *trans*-isomer. The relative intensities of the two methyl bands showed the *cis-trans* ratios to be 1 : 1 in the case of (IV) and 1 : 2 for (V).

The exocyclic α -proton in the 3-methyl compounds also gave rise to two clear signals [at 6.46 and 6.49 p.p.m. for (IV) and at 6.75 and 6.78 p.p.m. for (V)]. The isomer ratios found by this method agree with those estimated from the dipole moment studies.

A temperature-dependence study of both the methyl and the exocyclic α -proton absorptions showed no change up to 180 °C. The barrier to rotation about the exocyclic double bond is apparently high enough not to allow a significant exchange of the sites of the substituents below 180 °C.

An additional effect was observed in the temperature variation study of compounds (II) and (V). The methylene protons at positions 10 and 11 in both the 3-chloro- and the 3-methyl derivative resonate at 3.18 p.p.m. The signal is a well resolved AA'BB' multiplet at -55 °C, coalescing at room temperature and becoming a very sharp singlet at 112 °C. This allows an estimate of the inversion energy of the bridge carbon atoms: ΔG^\ddagger 15 kcal mol⁻¹.

Thus, in the cases studied, the Wittig-Horner reaction yields a mixture of two geometrical isomers. As the double bonds do not show a low energy barrier to rotation, the geometrical isomers must be distinct chemical species in solution.

¹⁰ B.P. 943,604/1963 (*Chem. Abs.*, 1964, **61**, P4294).

¹¹ I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.

EXPERIMENTAL

The synthesis of compounds (I)—(III) has been previously described.⁷

5-(4-Cyanobenzylidene)-3-methyl-5H-dibenzo[a,d]cycloheptene (IV).—A mixture of diethyl 4-cyanobenzylphosphonate (5.06 g, 0.02 mol), 3-methyl-5H-dibenzo[a,d]cycloheptene-5-one¹⁰ (2.2 g, 0.01 mol) and 50% sodium hydride (0.96 g, 0.02 mol) in dimethyl sulphoxide (56 ml) was heated at 100° for 24 h. The *product* was chromatographed on neutral alumina with benzene as eluant and recrystallized from cyclohexane; yield 80%, m.p. 179—180° (Found: C, 89.9; H, 5.5; N, 4.4. C₂₄H₁₇N requires C, 90.3; H, 5.3; N, 4.4%); $\bar{\nu}_{\max}$ (KBr) 2230, 1600, 1450, 1180, 910, 830, and 765 cm⁻¹; λ_{\max} (EtOH) 296 nm (log ϵ 4.41); δ (CDCl₃) 7.50—6.90 (1H, m), 6.91 (2H, s), 6.49 and 6.46 (each s, total 1H), and 2.42 and 2.18 p.p.m. (each s, total 3H).

5-(4-Cyanobenzylidene)-10,11-dihydro-3-methyl-5H-dibenzo[a,d]cycloheptene (V).—This was prepared analogously from 3-methyl-10,11-dihydro-5H-dibenzo[a,d]cyclohepten-5-one.¹⁰ The *product* was recrystallized from cyclohexane; yield 28%, m.p. 156—159° (Found: C, 90.1; H, 6.1; N, 4.4. C₂₄H₁₉N requires C, 89.7; H, 5.9; N, 4.4%); $\bar{\nu}_{\max}$ (KBr) 2235, 1600, 1450, 1180, 920, 820, and 760 cm⁻¹; λ_{\max} (EtOH) 305 nm (log ϵ 4.32); δ (CDCl₃) 7.50—6.90 (1H, m), 6.78 and 6.75 (each s, total 1H), 3.18 (4H, s), and 2.35 and 2.14 p.p.m. (each s, total 3H).

Thin-layer Chromatography.—The reaction products were chromatographed on plates coated with silver nitrate-silica gel (1 : 3), with light petroleum-ether (3 : 2) as developer. U.v. light revealed two spots of comparable magnitude in each case studied; R_F values: (I) 0.35, 0.47; (II) 0.37, 0.40; (III) 0.22, 0.34.

Dipole Moments.—The moments were measured by the heterodyne beat method and calculated according to the procedure of Halverstadt and Kumler,¹¹ as previously described.⁸ The data are summarized in Table 2.

Nuclear Magnetic Resonance.—The n.m.r. studies were carried out on a Varian HA 100D spectrometer at 100 MHz with probe temperature 31.5 °C. [²H]Chloroform was used as solvent at room and at lower temperatures, and perchlorobutadiene at elevated temperatures. In all measurements tetramethylsilane or hexamethyldisiloxane was used as internal standard.