Stereochemical outcome of McMurry coupling

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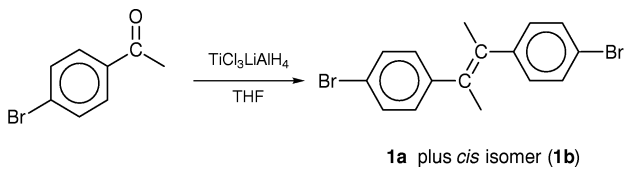
McMurry coupling of 4-bromoacetophenone using the product of reaction of lithium aluminium hydride and titanium trichloride in THF gives 2,3-bis(4-bromophenyl)-2-butenes in a *cis* : *trans* ratio of approximately 9 : 1. This unexpected result was confirmed by X-ray crystallography and resolves an inconsistency in earlier literature assignments. Coupling of 4-bromobenzophenone under the same conditions gives *cis* and *trans* isomers in an approximately 1 : 1 ratio.

2,3-Bis(4-bromophenyl)-2-butene (**1**) and 1,2-bis(4-bromophenyl)-1,2-diphenylethene (**2**) were required as monomers for the synthesis of poly(arylene vinylene)s *via* Yamamoto[1] and Suzuki[2] coupling procedures. Since the objective was to study the influence of vinylene geometry on polymer properties, pure *cis* and *trans* isomers of the monomers were required. We selected McMurry coupling of the appropriate bromoketones for these syntheses. This is a well established method and product stereochemistries have been assigned on the basis of melting points and spectroscopic analysis. Unfortunately the literature concerning such assignments is inconsistent. In this paper we report the synthesis, separation and purification of these compounds. Isomer structures were assigned unambiguously by means of X-ray crystallography.

2,3-Bis(4-bromophenyl)-2-butenes

The synthesis of 2,3-bis(4-bromophenyl)-2-butenes (**1**) (Scheme 1) was carried out by McMurry coupling of 4-bromoacetophenone. The product was recovered as colourless crystals. The ^{1}H NMR spectrum of this product shows two singlet peaks attributed to methyl hydrogens in *cis* and *trans* isomers, at 2.12 and 1.84 ppm, with the former peak corresponding to the major product; however, it is not certain which one is which.

Inamoto *et al.* have discussed the stereochemical assignment of 2,3-bis(4-bromophenyl)-2-butenes.[3] In an attempt to solve this assignment problem, the chemical shifts of the methyl hydrogens for a series of substituted αα′-dimethylstilbenes were measured. The shielding effect experienced by the methyl groups, which arises from the π electron current in the phenyl groups, varies with isomer geometry. Calculations were made in an attempt to correlate the stereochemistry of the various substituted αα′-dimethylstilbenes with the chemical shifts of the methyl hydrogens. On this basis it was suggested that methyl hydrogens in *trans* isomers absorb at a higher field than those in *cis* isomers. Also it was found that the isomers assigned *trans* stereochemistry on this basis had higher melting points than the corresponding isomers assigned *cis* stereochemistry, which is reasonable and was not unexpected. In the case of 2,3-bis(4-bromophenyl)-2-butene, the melting points of *cis* and *trans* isomers were recorded at 82 and 146 °C, respectively. At least one group,[4] has supported the assignment made by Inamoto *et al.*[3]



1a plus *cis* isomer (**1b**)

Scheme 1 Synthesis of 2,3-bis(4-bromophenyl)-2-butenes *via* the McMurry reaction

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However, in 1978 McMurry and co-workers reported that the synthesis of 2,3-diphenyl-2-butene from acetophenone gave a 9 : 1 mixture of isomers.[5] In the ^{1}H NMR spectra the methyl hydrogen in major and minor products displayed resonances at 2.14 and 1.87 ppm, respectively. According to the earlier assignments,[3,4] this was a mixture of 90% *cis* and 10% *trans* isomers; however, McMurry and co-workers believed that these assignments were almost certainly wrong since analogous compounds such as stilbene and stilbestrol [3,4-bis(4-hydroxyphenyl)-3-hexene] were known to prefer a *trans* geometry. This argument was supported by Richardson in 1981.[6] Subsequently, Leimner and Weyerstahl[7] concluded that for McMurry coupling of alkylaryl ketones *cis* isomers predominated for sterically undemanding alkyl groups, whereas bulky alkyl groups favoured the *trans* isomers. These reasonable and reasonably convincing assignments were based on the analysis of ^{1}H NMR spectra.

We have been able to provide an unambiguous resolution of this inconsistency in the literature by obtaining the crystal structure of one of the isomers. Fig. 1 presents the crystal structure of the major product which is the *cis* isomer (**1b**).

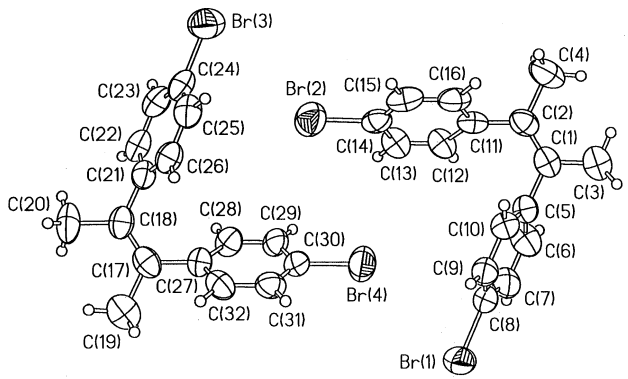


Fig. 1 Two independent molecules of *cis*-2,3-di(4-bromophenyl)-2-butene **1b** (showing 50% displacement ellipsoids). Bond distances/Å: C(1)—C(2) 1.329(10), C(1)—C(5) 1.491(1), C(2)—C(11) 1.497(10), C(1)—C(3) 1.513(10), C(2)—C(4) 1.542(1), C(17)—C(18) 1.343(10), C(17)—C(27) 1.493(10), C(18)—C(21) 1.486(10), C(17)—C(19) 1.536(10), C(18)—C(20) 1.507(9), Br—C average 1.901(8)

This isomer shows a methyl hydrogen resonance at 2.12 ppm. The asymmetric unit of **1b** contains two molecules (Fig. 1) with similar geometry and molecular conformation, corresponding to a local approximate C_2 symmetry (phenyl rings are inclined with respect to the mean olefinic plane in the same direction, by 54–58°). Both molecules show an insignificant torsion angle around the double bond (5.2 and 2.9°, *cf.* 3.9° in the parent *cis*-2,3-diphenyl-2-butene,[8] **3**). This bond is marginally longer [mean 1.336(10) Å] than the standard C=C distance (from X-ray data, 1.31 Å)[9] and essentially the same as in **3** [1.343(4) Å]. The ^{1}H and ^{13}C NMR spectra are consistent with the assigned structure.

Thus, it is confirmed that the formation of the *cis* isomer is favoured in the synthesis of 2,3-bis(4-bromophenyl)-2-butenes *via* the McMurry reaction. The *cis* isomer was found to constitute about 88% of the recovered product mixture before separation of the isomers. Since the isomer with the methyl hydrogen resonance at 2.12 ppm in ^{1}H NMR spectrum turned out to be the *cis* isomer, this result confirms Inamoto's hypothesis that the methyl hydrogens in the *trans* isomer of 2,3-bis(4-bromophenyl)-2-butene absorb at higher field than those in the *cis* isomer. The ^{13}C NMR spectrum was consistent with the assigned structure.

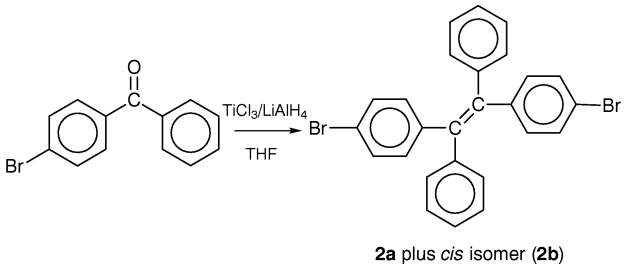
This work provides unambiguous confirmation of the assignment first made by Inamoto and supported by the work of Leimner and Weyerstahl and proves the rather surprising result that the *cis* isomer is the major product of McMurry coupling of acetophenones.

1,2-Bis(4-bromophenyl)-1,2-diphenylethenes

A similar procedure to that described above was used for the synthesis of 1,2-bis(4-bromophenyl)-1,2-diphenylethene (**2**) from 4-bromobenzophenone, see Scheme 2. The product was a mixture of *cis* and *trans* isomers, in this case the selectivity was less and the 'major' isomer constituted 56% of the yield before separation of the isomers. Both isomers were obtained, with a purity in excess of 98% as measured by ^{1}H NMR spectroscopy, by repeated recrystallisation from a 2 : 3 mixture of toluene and ethanol. The assignments of the *cis* and *trans* isomers were made on the basis of the crystal structure obtained for a sample of the 'major' isomer, see Fig. 2.

Crystalline molecule **2a** has an approximate local C_2 symmetry. The planes of the unsubstituted phenyl rings A and B (Fig. 2) form similar dihedral angles of 54.8 and 56.9°, respectively, with the bonding (sp^2) planes of C(1) and C(2). For the bromo-substituted rings C and D, the corresponding dihedral angles are 36.4° and 34.6°, respectively. Owing to steric overcrowding, the torsion angle around the central double bond (11.9°) and stretching of this bond [1.357(7) Å] are larger than in **1b**, but similar to those observed in other tetraphenylethene derivatives.[10] The only unusual intermolecular contact is Br(1)···C(12′) 3.35 Å, which is considerably shorter than the standard distance of 3.63 Å.[11]

In contrast to the case of 2,3-bis(4-bromophenyl)-2-butene, in which the *cis* isomer forms the major product, the *trans* isomer was very slightly favoured in the synthesis of 1,2-bis(4-bromophenyl)-1,2-diphenylethene. Fig. 3 presents the ^{1}H NMR spectra of both *cis*- and *trans*-1,2-bis(4-bromophenyl)-1,2-diphenylethene.



2a plus *cis* isomer (**2b**)

Scheme 2 Synthesis of 1,2-bis(4-bromophenyl)-1,2-diphenylethenes

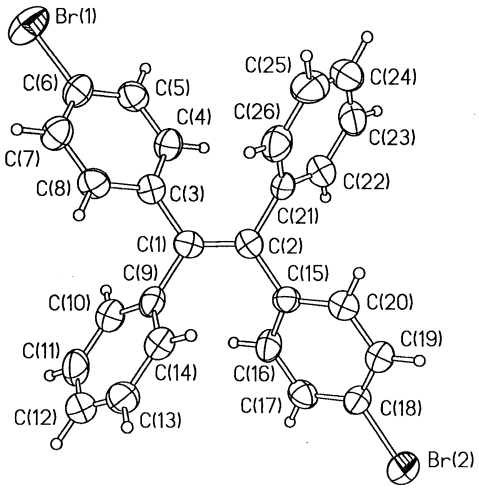


Fig. 2 Molecular structure of the major product *trans*-1,2-bis(4-bromophenyl)-1,2-diphenylethene **2a** (showing 50% displacement ellipsoids). Bond distances/Å: C(1)—C(2) 1.357(7), C(1)—C(3) 1.497(7), C(1)—C(9) 1.504(8), C(2)—C(15) 1.505(7), C(2)—C(21) 1.488(8), Br(1)—C(6) 1.903(6), Br(2)—C(18) 1.902(6)

Experimental

4-Bromobenzophenone, 4-bromoacetophenone, lithium aluminium hydride and titanium trichloride were purchased from Aldrich. THF was purchased from BDH. All reagents were used without further purification except 4-bromoacetophenone which was recrystallised from ethanol twice. THF was dried by distillation from sodium metal/sodium benzophenone ketyl radical prior to use.

^{1}H and ^{13}C NMR spectra were recorded using a Varian 400 MHz spectrometer and were referenced to Me_4Si. IR Spectra were recorded using a Perkin–Elmer 1600 series FTIR spectrometer.

X-Ray crystallography

Single-crystal diffraction experiments were carried out at room temperature on a Siemens SMART 3-circle diffractometer, equipped with a CCD area detector. Graphite-monochromated Mo-Kα radiation was used (λ = 0.71073 Å). A full hemisphere of the reciprocal space up to 2θ = 50° was scanned by ω in 0.3° frames. The integrated intensities were corrected for absorption: in **1b** by a semi-empirical method based on Laue equivalents with different ψ angles, in **2a** by a numerical integration method, based on measured crystal shape and face-indexing. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 of

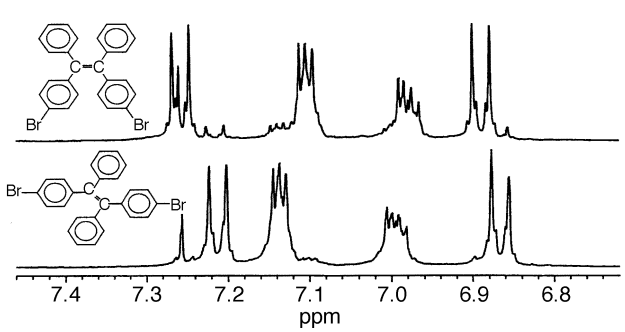


Fig. 3 ^{1}H NMR spectra of *cis*- (top) and *trans*-1,2-bis(4-bromophenyl)-1,2-diphenylethene (bottom)

all positive data (all non-hydrogen atoms with anisotropic displacement parameters, H atoms in 'riding' model), using SHELXTL software.[12] Crystal data and experimental details are listed in Table 1, atomic coordinates are deposited at the Cambridge Crystallographic Data Centre (CCDC reference number 440/063).

Synthesis of 2,3-bis(4-bromophenyl)-2-butenes

Titanium trichloride (11.70 g, 76 mmol) and dry THF (150 ml) were transferred under a dry oxygen free nitrogen atmosphere into a two-necked round-bottomed flask (250 ml) fitted with a condenser, dry nitrogen inlet and a magnetic stirrer. The dry oxygen-free nitrogen atmosphere was maintained through the experiment until destruction of excess reagents. After immersing the flask into an ice bath, $LiAlH_4$ (1.43 g, 38 mmol) was slowly added over a period of approximately 30 min while stirring rapidly. The mixture was refluxed for 1 h. The resultant black slurry was allowed to cool to room temperature and 4-bromoacetophenone (7.55 g, 38 mmol) was added. After a further 20 h at reflux, the mixture was cooled in an ice bath and dilute HCl (100 ml, 2 M) was added slowly to quench the reaction and destroy excess coupling reagents. The product was then extracted into chloroform (3 × 100 ml); solvent was evaporated from the combined extracts to give a yellow oil which was eluted through neutral alumina using hexane to give as a colourless oil a mixture of *cis*- and *trans*-2,3-bis(4-bromophenyl)-2-butene (3.35 g, 51 mol% yield w.r.t. 4-bromoacetophenone). Repeated recrystallisation from hexane gave the pure *cis*-2,3-bis(4-bromophenyl)-2-butene, mp 80.2–81.8 °C (lit.[3] 82 °C); found: C, 52.39; H, 3.59; $C_{16}H_{14}Br_2$ requires C, 52.49; H, 3.85%. ^{1}H NMR (δ, $CDCl_3$, 400 MHz): 7.22 (pseudo d, 4, aromatic CH), 6.81 (pseudo d, 4, aromatic CH) and 2.12 (s, 6, CH_3). ^{13}C NMR (δ, $CDCl_3$, 100 MHz): 21.4 (CH_3), 119.7 (CBr), 130.8 (aromatic CH), 130.9 (aromatic CH), 132.5 (alkylidene C) and 143.1 (aromatic C). FTIR (KBr disc, ν_{max}/cm^{-1}): 2987, 2915, 1584, 1482, 1392, 1074, 1007, 827, 725, 559, 525, 476. The same procedure was applied to isolate the pure *trans*-2,3-bis(4-bromophenyl)-2-butene, mp 140.3–142.1 °C (lit.[3] 146 °C). The product was characterised by mass spectrometry; $M + 1$ ion = 365 determined by EI mass spectrometry: ^{1}H NMR (δ, $CDCl_3$), 7.49 (pseudo d, 4, aromatic CH), 7.14 (pseudo d, 4, aromatic CH) and 1.84 (s, 6, CH_3); ^{13}C NMR (δ, $CDCl_3$, 100 MHz), 22.3 (CH_3), 120.2 (CBr), 130.0 (aromatic CH), 131.4 (aromatic CH), 132.6 (alkylidene C) and 142.9 (aromatic C); FTIR (KBR disc, ν_{max}/cm^{-1}), 2940, 2914, 1583, 1486, 1443, 1391, 1069, 1005, 828, 784, 719, 608, 527.

Table 1 Crystal data and X-ray experiment parameters

	1b	**2a**
Formula	$C_{16}H_{14}Br_2$	$C_{26}H_{18}Br_2$
M	366.1	490.2
Crystal size/mm	0.35 × 0.35 × 0.25	0.28 × 0.20 × 0.06
Colour	colourless	colourless
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	12.226(1)	10.692(1)
b/Å	15.976(1)	9.191(1)
c/Å	15.792(1)	22.641(1)
β/°	98.38(1)	102.47(1)
U/Å^3	3051.6(4)	2172.4(3)
Z	8	4
d_{calcd}/g cm^{-3}	1.59	1.50
μ(Mo-Kα)/cm^{-1}	52.9	37.4
Data total	17930	12604
Data used (unique)	4184	3228
R_{int} before, after abs.corr.	0.134, 0.082	0.166, 0.090
Transmission max,min	0.291, 0.185	0.810, 0.418
Data observed, $J > 2\sigma(I)$	2682	2270
Variables refined	326	254
R_1 (obs. data)	0.067	0.062
wR_2 (obs. data)	0.100	0.092
Goodness of fit	1.14	1.15
$\Delta\rho_{max,min}$/e Å^{-3}	0.46, −0.45	0.40, −0.54

Synthesis of 1,2-bis(4-bromophenyl)-1,2-diphenylethenes

Lithium aluminium hydride (1.45 g, 38 mmol) was slowly added to a slurry of titanium trichloride (11.80 g, 76 mmol) in dry THF (150 ml) under a dry nitrogen atmosphere at about 0 °C while stirring rapidly. The mixture was then refluxed for 1 h. At room temperature, 4-bromobenzophenone (10.00 g, 38 mmol) was added and this mixture was refluxed for 20 h. The reaction was quenched by adding dilute hydrochloric acid (2 M, 100 ml) into the mixture at room temperature while stirring. The product was extracted into chloroform (3 × 50 ml), washed with brine and dried over magnesium sulfate. The solvent was evaporated from the combined extracts and the residual yellow oil was reprecipitated into methanol. The precipitate was collected and dried to give a *cis*/*trans* mixture of 1,2-bis(4-bromophenyl)-1,2-diphenylethene (7.30 g, 78 mol yield w.r.t. 4-bromobenzophenone). Multiple recrystallisation from a mixture of ethanol and toluene (3 : 2, v/v) yielded the pure *cis*-1,2-bis(4-bromophenyl)-1,2-diphenylethene, mp 214.3–214.6 °C. The product was characterised by: ^{1}H NMR see Fig. 3; ^{13}C NMR (δ, $CDCl_3$, 100 MHz) 120.8 (CBr), 126.8 (aromatic CH), 127.8 (aromatic CH), 131.1 (aromatic CH), 131.2 (aromatic CH), 132.9 (aromatic CH), 140.2 (alkylidene C), 142.3 (aromatic C) and 142.9 (aromatic C). The same procedure was applied to isolate the pure *trans*-1,2-bis(4-bromophenyl)-1,2-diphenylethene, mp 214.5–214.9 °C; $M + 1$ ion = 490 determined by EI mass spectrometry; found: C, 63.82; H, 3.49; $C_{26}H_{18}Br_2$ requires C, 63.70; H, 3.70%; molecular mass, 488 (2Br), ^{1}H NMR see Fig. 3, ^{13}C NMR (δ, $CDCl_3$, 100 MHz) 120.6 (CBr), 126.9 (aromatic CH), 128.0 (aromatic CH), 130.9 (aromatic CH), 131.2 (aromatic CH), 132.8 (aromatic CH), 140.2 (alkylidene C), 142.3 (alkylidene C) and 142.8 (alkylidene C).

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