Synthesis of 1,1'-Biindenes and 3,3'-Biindenes

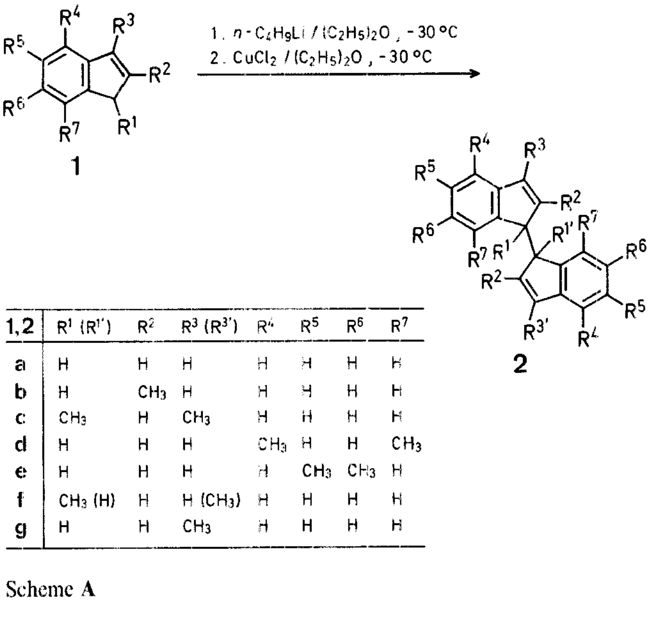
Pierre Nicolet,** Jean-Yves Sanchez, Ahmed Benaboura, Marc J. M. Abadie*

Laboratoire de Chimie Macromoléculaire, Université des Sciences et de la Technologie Houari Boumediene, Dar El Beida, BP no. 9, Alger

1,1'-Biindenes **2**, conveniently prepared from indenyllithiums by treatment with copper(II) chloride, are quantitatively isomerized to the corresponding 3,3'-biindenes **3** by heating in triethylamine/pyridine. Both *d, l* and *meso* isomers of **2** react to form **3**; the rate of reaction of the *meso* form, however, is substantially faster.

The bis[1-indenyl], isolated for the first time by Grignard and Courtot,[1] was later prepared with a good yield by Marechal et al.[2] However, the methods used are either inconvenient (use of BrCN) or require long times (48 h minimum).

We report here a simple and rapid method for preparation of 1,1'-biindenes in synthetically useful yields within 2 h and without the necessity of changing the reaction solvent. Indenes **1** react with *n*-butyllithium to form the intermediate indenyllithiums which give 1,1'-biindenes **2** on treatment with copper(II) chloride (Scheme **A**).



1,2	R^1 ($R^{1'}$)	R^2	R^3 ($R^{3'}$)	R^4	R^5	R^6	R^7
a	H	H	H	H	H	H	H
b	H	CH_3	H	H	H	H	H
c	CH_3	H	CH_3	H	H	H	H
d	H	H	H	CH_3	H	H	CH_3
e	H	H	H	H	CH_3	CH_3	H
f	CH_3 (H)	H	H (CH_3)	H	H	H	H
g	H	H	CH_3	H	H	H	H

Scheme A

This method was applied successfully to the synthesis of the 1,1'-biindenes **2a–e** (Table). The original indenes **1a–e** are all symmetrical ($R^1 = R^3$, $R^4 = R^7$, $R^5 = R^6$), i.e. they remain identical after an eventual shift of the double bond. There is, therefore, the possibility of easily attaining a new series of compounds of interest in the field of macromolecules, based on the fact that **2a** is known to react to give high cationic polymers which have thermostable character.[3]

On the other hand, the coupling of non-symmetrically substituted indenes (**1f, g**) leads to a mixture of positional isomers. Thus, the same mixture of isomers **2f** and **2g** (Table) is obtained irrespective of whether 1-methylindene (**1f**) or 3-methyl indene (**1g**) is used.

In spite of the good overall yield, the difficulties associated with the separation of positional isomers makes this method less suitable for the coupling of the non-symmetrically substituted indenes **1f, g**.

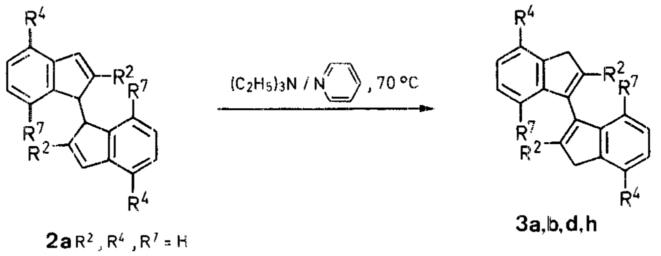
We also report a rapid preparation of 3,3'-biindenes **3** from some 1,1'-biindenes **2** which proceeds in good yield (95%) (Scheme **B**).

To our knowledge, no selective method exists up to now for the synthesis of 3,3'-biindenes. The known products have been obtained by one of the following routes:

A bimolecular reduction of indanones by aluminium amalgam, followed by acidic dehydration;
B reaction of 1-indanone with 1-indenylmagnesium bromide, followed by dehydration with hydrogen chloride gas;
C as in (b), but with thermal dehydration.

Routes A[5,6] and B[7] lead mostly to a mixtures of 3,3'-biindenes and indanylidene-indenes. By route C,[8] the yield does not exceed 60%.

We have obtained complete conversion of 1,1'-biindenes **2** into 3,3'-biindenes **3** (Table) in the presence of triethylamine with pyridine as solvent at 70 °C. Moreover, the compounds **3** may be obtained from *meso-*, *d, l* or a mixture of *meso-* and *d, l*-isomers of 1,1'-biinderes **2**.



2a $R^2, R^4, R^7 = H$
b $R^2 = CH_3$; $R^4, R^7 = H$
d $R^2 = H$; $R^4, R^7 = CH_3$
h $R^2 = H$; $R^4, R^7 = Cl$
(*d, l* and/or *meso*)

Scheme **B**

Several comments should be made regarding this reaction. Although both *meso-* and *d, l*-isomers of **2** are converted to 3,3'-biindenes **3** under the described conditions, the reactivity of the two diastereomers is substantially different. For example, the rate of isomerization of the *meso*-isomer of **2d** is 40 times greater than that of the *d, l*-isomer.

In all reactions, followed by ^1H-NMR spectrometry, there is no evidence for the existence of a 1,3'-biindene as an intermediate product corresponding to a change in position of only one double bond. Therefore, we must assume that, under the experimental conditions, the change in position of the second double bond occurs in a fast step.

Contrary to the isomerization of the 1-alkylindenes,[9] which is often an equilibrium reaction, that of 1,1'-biindenes is always complete. This should be attributed to the increased stability of the 3,3'-structure as compared to the 1,1'-structure.

1,1'-Biindenes 2; General Procedure:

A solution of indene **1** (0.25 mol) in ether (40 ml) is added to a stirred and cooled (−30 °C) solution of *n*-butyllithium (22 g) in ether (100 ml). After 30 min. anhydrous copper(II) chloride (35 g) is added, whereby the mixture becomes a black coloration. After 30 min, the reaction is quenched by addition of a small quantity of ice/water, until the black colour completely disappears. The stirring is stopped and the organic phase is decanted. After extraction with ether (3 × 100 ml) and washing with water (2 × 50 ml), the organic phase is filtered on active charcoal, dried with magnesium sulfate, and the ether is removed under vacuum. The crude products are recrystallized from methanol to give white needles. The *meso-* and *d, l*-forms are separated by fractional recrystallization from methanol.

1,3'-Dimethyl-bis[1-indenyl] (**2f**) and 3,3'-dimethyl-bis[1-indenyl] (**2g**) are obtained from 1-methylindene (**1f**) or 3-methylindene (**1g**) as a yellow oil (overall yield: 95%) mainly consisting of **2f** (about 70%) and **2g**

Table. 1.1′-Biindenes **2** and 3,3′-Biindenes **3**

Product	Overall Yield (%)	*d, l*/*meso* ratio[a]	Molecular Formula[b]	MS[c] *m/e* (M^+)	Isomer Form[d]	Yield (%)	m.p. (°C) (Lit. m.p.)	^{1}H-NMR (CCl_4, TMS)[e] δ (ppm)
2a	95	70 : 30	$C_{18}H_{14}$ (230.3)	230	**d,l-2a**	50	99° (99°)[2]	4.00 (s, 2H); 5.65 (d, 2H, *J* = 6 Hz); 6.45 (d, 2H, *J* = 6 Hz); 6.9–7.6 (m, 8H)
					meso-**2a**	10	77° (77.5°)[4]	3.95 (s, 2H); 6.15 (d, 2H, *J* = 6 Hz); 6.60 (d, 2H, *J* = 6 Hz); 6.7–7.3 (m, 8H)[g]
2b	95	A : 8 = 90 : 10[f]	$C_{20}H_{18}$ (258.4)	258	A-2*b*[f]	70	118°	1.80 (s, 6H); 3.80 (s, 2H); 6.35 (s, 2H); 6.6–7.1 (m, 8H)
2c	95	A : B = 50 : 50[f]	$C_{22}H_{12}$ (286.4)	286	A-**2c**[f]	30	130°	1.15 (s, 6H); 2.00 (d, 6H, *J* = 2 Hz); 6.00 (q, 2H, *J* = 2 Hz); 6.7–7.1 (m, 8H)
					B-**2c**	20	115°	1.40 (s, 6H); 2.05 (d, 6H, *J* = 2 Hz); 5.90 (q, 2H, *J* = 2 Hz); 6.8–7.3 (m, 8H)
2d	95	50 : 50	$C_{22}H_{22}$ (286.4)	286	*d,l*-**2d**	35	129°	2.30 (s, 6H); 2.60 (s, 6H); 4.30 (s, 2H); 5.50 (d, 2H, *J* = 6 Hz); 6.50 (d, 2H, *J* = 6 Hz); 6.80 (s, 4H)
					meso-**2d**	10	69°	1.90 (s, 6H); 2.30 (s, 6H); 4.15 (s, 2H); 6.05 (d, 2H, *J* = 6 Hz); 6.55 (d, 2H, *J* = 7 Hz); 6.60 (d, 2H, *J* = 6 Hz); 6.75 (d, 2H, *J* = 7 Hz)
2e	95	50 : 50	$C_{22}H_{22}$ (286.4)	286	*d,l*-**2e**	35	140°	2.30 (s, 12H); 3.95 (s, 2H); 5.55 (d, 2H, *J* = 6 Hz); 6.45 (d, 2H, *J* = 6 Hz); 6.95 (s, 2H); 7.20 (s, 2H)
					meso-**2e**	15	136°	2.15 (s, 6H); 2.25 (s, 6H); 3.85 (s, 2H); 6.05 (d, 2H, *J* = 6 Hz); 6.50 (d, 2H, *J* = 6 Hz); 6.50 (s, 2H); 6.90 (s, 2H)
2f + **2g**	95	70 : 20	$C_{20}H_{18}$ (258.4)	258	A-**2f** A-**2g**	20	147°	1.5 (s, 3H); 2.1 (m, 3H); 3.7 (m, 1H); 5.8–7.5 (m, 11H)
					A-**2g**	–		2.00 (d, 6H, *J* = 1 Hz); 3.95 (s, 2H); 5.35 (q, 2H, *J* = 1 Hz); 6.9–7.5 (m, 8H)
3a	95	–	$C_{18}H_{14}$ (230.3)	230	–	–	131° (131°)[8]	3.45 (d, 4H, *J* = 1 Hz); 6.55 (t, 2H, *J* = 1 Hz); 7.0–7.6 (m, 8H)
3b	95	–	$C_{20}H_{18}$ (258.4)	258	–	–	158°	2.10 (s, 6H); 3.50 (s, 4H); 6.8–7.5 (m, 8H)
3d	95	–	$C_{22}H_{22}$ (286.4)	286	–	–	178°	1.95 (s, 6H); 2.35 (s, 6H); 3.25 (d, 4H, *J* = 2 Hz); 6.30 (t, 2H, *J* = 2 Hz); 6.80 (s, 4H)
3h	95	–	$C_{18}H_{10}Cl_4$ (361.1)	368	–	–	217°	3.40 (d, 4H, *J* = 2 Hz); 6.35 (t, 2H, *J* = 2 Hz); 7.00 (s, 4H)

[a] Determined by ^{1}H-NMR spectrometry.
[b] Satisfactory microanalyses obtained: C ±0.20, H ±0.30, Cl ±0.30 (Service de microanalyses, INSCIR, BP no. 8, F-76130 Mont-Saint-Aignan).
[c] Mass spectra were recorded by Prof. Granger, U.E.R. des Sciences, Place E. Blondel, F-76130 Mont-Saint-Aignan.
[d] Structures proposed by analogy to ^{1}H-NMR spectrum to **2a**.
[e] The ^{1}H-NMR spectra were recorded on a Varian EM 360 A spectrometer.
[f] Structures of isomers not assigned unequivocally.
[g] DMSO-d_6 at 120 °C.

(about 20%) by ^{1}H-NMR; after crystallization from methanol **2f** is obtained pure (white needles, yield: 20%) and **2g** is obtained as a 70 : 30 mixture with **2f**.

3,3′-Biindenes 3; General Procedure:

A solution of 1,1′-biindene **2** (0.05 mol) and triethylamine (28 ml) in pyridine (100 ml) is refluxed for 4 h. Pyridine and triethylamine are removed under vacuum. The residue is extracted with ether (100 ml), the ether phase, washed with a dilute hydrochloric acid (10%) until neutral pH, is dried with magnesium sulfate, and evaporated. Afterwards, the solid product is washed with methanol and recrystallized from acetic anhydride.

Received: 9 December 1980
(Revised form: 28 April 1986)

* To whom correspondence should be addressed. Present address: Laboratoire d'Etude des Matériaux Polymères, Université des Sciences et Techniques du Languedoc, F-34060 Montpellier, France

** Present address: Laboratoire de spectrochimie Moléculaire, UER Chimie, F-44072 Nantes, France

(1) Grignard, V., Courtot, C. *C. R. Acad. Sci.* **1912**, *154*, 362.
(2) Marechal, E., Basselier, J.J., Sigwalt, P. *Bull. Soc. Chim. Fr.* **1964**, 1740.
(3) Nicolet, P. *J. Macromol. Sci. Chem.* **1977**, *11*, 577.
(4) Lustenberger, P. *Z. Kristallogr.* **1979**, *150*, 235.
(5) Kemp, W., Spanswick, J. *J. Chem. Soc.* **1972**, 151.
(6) Majerus, G., Yax, E., Ourisson, G. *Bull. Soc. Chim. Fr.* **1967**, 4147.
(7) Courtot, C. *Ann. Chim.* **1915**, *9*, 4.
(8) Marechal, E., Sigwalt, P. *Bull. Soc. Chim. Fr.* **1966**, 1075.
(9) Weidler, A.M. *Acta Chem. Scand.* **1963**, *17*, 2724.