PHOTOCHEMISTRY WITH CIRCULARLY POLARIZED LIGHT—III

SYNTHESIS OF HELICENES USING BIS(ARYLVINYL) ARENES AS PRECURSORS

A. MORADPOUR†, H. KAGAN†*, M. BAES‡, G. MORREN‡ and R. H. MARTIN‡*

†Laboratoire de synthèse asymétrique (ERA CNRS No 070559), Université de Paris-Sud, Centre d'Orsay, 91405-Orsay, France

‡Service de Chimie Organique, Faculté des Sciences, Université Libre de Bruxelles, 50 Av. F.D. Roosevelt B-1050 Bruxelles, Belgique

Abstract—A systematic study of the photochemical ring-closure of bis(arylvinyl)arenes, using circularly polarized light, is described and commented. In the two series of compounds **5a–e** and **6a–e**, the observed optical yields follow a similar trend; no asymmetric syntheses were observed in the case of the higher benzologues of [10] helicene, using a 290–370 nm irradiation band, circularly polarized at 313 nm.

We have described, in earlier publications, the first asymmetric photosyntheses of [6], [8] and [9] helicene, induced by circularly polarized light.[1]

Soon after, Bernstein *et al.* published the results of closely related investigations, including a study of the structural and wavelength dependence of the induced optical yields.[2]

We now wish to report the results of a recent research on the synthesis of helicenes using bis(arylvinyl)arenes as precursors and circularly polarized light for the photochemically induced ring-closure step.

The "double photocyclisation" process has indeed proven very convenient for the preparation of [6] and [7] helicene, starting from readily accessible chemicals,[3] and for the synthesis of the higher benzologues, up to [14] helicene inclusive.[4]

The study of the photocyclisation of dienes **1** and **3** (Scheme 1), two precursors of [6] helicene, was undertaken first. Both **1** and **3** led to [6] helicene with a specific rotation of $[\alpha]_D + 1 \cdot 9 \pm 0 \cdot 4°$ (left circularly polarized light = LCP). This value is quite comparable to the value obtained ($[\alpha]_D + 1 \cdot 9 \pm 0 \cdot 5°$) by the photocyclisation (LCP) of the 1,2-diarylethylene **4**.[1c] There is thus strong evidence that the double photocyclisation of **1** leading to [6] helicene proceeds via the intermediate **4** rather than the intermediate **2**. This assertion is further strengthened: (a) by the fact that only **4** could be detected by GLC in the

course of the photolysis, (b) by the prediction of the regio-selectivity of the first cyclisation based on the $\Sigma F_{r,s}^*$ (*vide infra*).§

A systematic study of two homologous series was then undertaken. The first one, **5b→5e**, derives from the 1,2-diarylethylene **4** (**5a**, R = H), a precursor of [6] helicene, the second one, **6b→6e**, is related to the 1,2-diarylethylene **6a**(R = H), a precursor of [8] helicene. Both **5a** and **6a** were shown previously to give unequivocal asymmetric syntheses using circularly polarized light, a higher optical yield being observed in the case of **6a**. Our present results are listed in Table 1.

In both series, the trend of the structural dependence of the induced optical yields and the failure to observe asymmetric syntheses in the case of the higher benzologues, require special attention. Different hypotheses could be put forward to explain these results. However, rather than speculate on inadequate data, we prefer to leave the question open.

Regioselectivity of the first photocyclisation. In the double photocyclisations of **5e**, **6c**, **6d** and **6e**, it is the first cyclisation which determines the course of the induced asymmetric syntheses. This follows from the fact that in the two possible 1,2-diarylethylenes intermediates resulting from the first cyclisation, the newly formed helicene structures ([6], [7] or [8]) are known to be photo-stable towards racemisation under the experimental conditions used.[9]
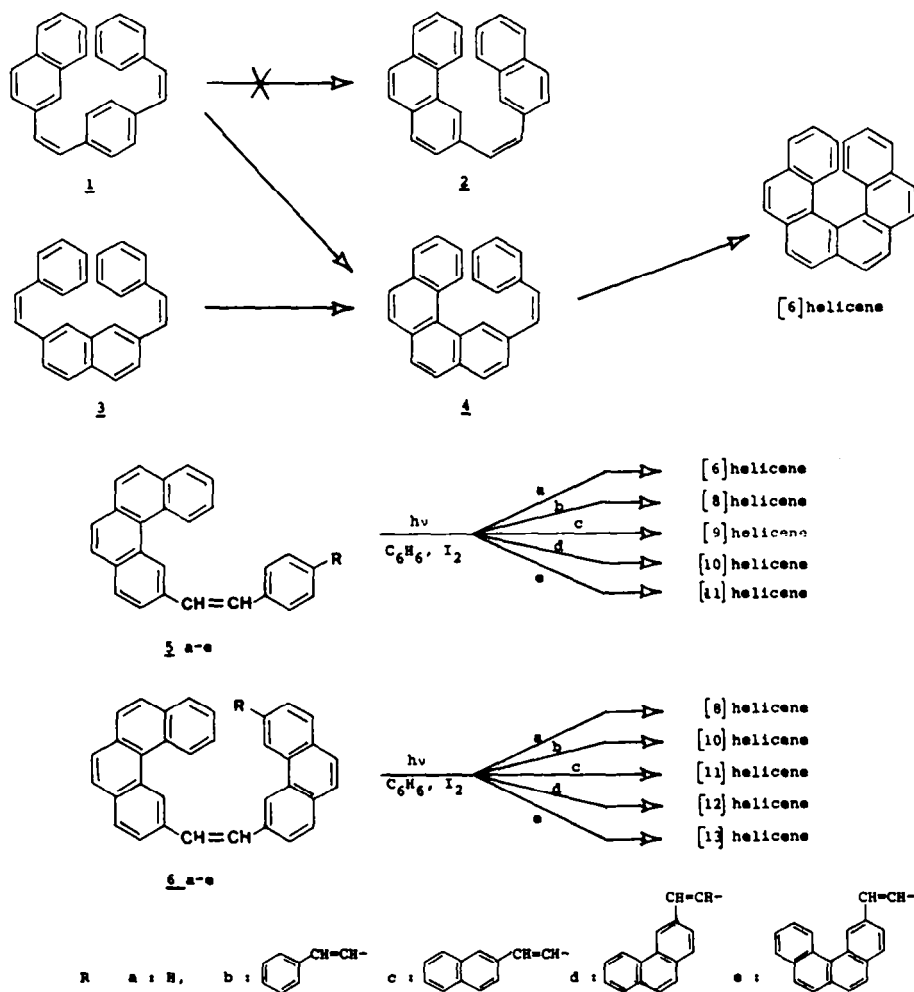
In the case of **5b** and **5c**, either the first or the second photocyclisation will be responsible of the induced asymmetric syntheses, depending on the course of the first photocyclisation. The remaining cases, namely **5d** and **6d**, are more ambiguous as they can give rise to a [5] helicene structure which is known to racemise at room temperature.[10]

We have therefore calculated the $\Sigma F_{r,s}^*$,[1] for the first cyclisation of the bis(arylvinyl)arenes used in this work. The results are listed in Table 2.

By *assuming* that the photocyclodehydrogenations take place preferentially between the two *ortho* carbon

---

§The photocyclisation of **1** leading to **4** could also be rationalised by assuming that the energy absorbed is essentially localised in the more condensed aromatic system (naphthalene in the case of **1**). It should however be recalled that this point of view, adopted by some authors[3,2a], was strongly controversed by Kluger *et al.*[6] A safe prediction or a correct interpretation of the observed results, could only be based on a quantitative treatment of all the factors involved in these multi-step processes (relative rates of the reversible and non-reversible steps leading to different isomers, relative quantum yields of the photochemical steps, steric factors. . .).

[1]$\Sigma F_{r,s}^*$ = sum of the free-valence indices in the first excited state of the carbon atoms between which cyclisation could occur.

A. MORADPOUR *et al.*

Scheme 1.

R   a : H,   b : (phenyl)CH=CH−   c : (naphthyl)CH=CH−   d : (phenanthryl)CH=CH−   e :

Table 1. Photochemical ring-closure of the bis(arylvinyl)arenes **5a-e** (LCP) and **6a-e** (RCP)[a]

Bis(arylvinyl) arene	Helicene obtained	Chemical yield %	Specific rotation $[\alpha]_D$ %	Approximate optical yield %	$[\alpha]_D^{max}$
5a	[6]	85	$+1.9 \pm 0.5°$	0.05	3640°[7]
5b	[8]	30	$+10.0 \pm 1.5°$	0.15	6700[8)b]
5c	[9]	50	$+31.8 \pm 1.5°$	0.42	7500[8)b]
5d	[10]	20	$+5.1 \pm 3°$	0.06	8300[9]
5e	[11]	60	$+0 \pm 1°$	0	
6a	[8]	85	$-31.2 \pm 1.5°$	0.46	6700[8)b]
6b	[10]	30	$-2.4 \pm 0.5°$	0.03	8300[9]
6c	[11]	80	$0 \pm 1°$	0	
6d	[12]	30	$0 \pm 1°$	0	
6e	[13]	40	$0 \pm 1°$	0	

a) Irradiations were performed in pyrex, using a 290-370 nm
irradiation band, as already described.

b) The $[\alpha]_D^{max}$ used in this work and the $[\alpha]_{579}^{max}$ reported in
(8), were determined on the same samples.

Table 2.

Precursor	$\Sigma F^{\bullet}_{r,s}$	$\Sigma F^{\bullet}_{r,s}$ values for the photocyclisations leading to : the less condensed aromatic system	$\Sigma F^{\bullet}_{r,s}$	the more condensed aromatic system
1	0.9525	Phenanthrene	1.0662	Benzo [c] phenanthrene
3	1.1475	Benzo [c] phenanthrene	-	-
5a	1.165[b)	[6] Helicene	-	-
5b	0.9489	Phenanthrene	1.0418	[6] Helicene
5c	1.0445	Benzo [c] phenanthrene	1.0283	[6] Helicene
5d	1.0114	[5] Helicene	1.0223	[6] Helicene
5e	1.024	[6] Helicene	-	-
6a	1.1501[b)	[8] Helicene	-	-
6b	1.0006	[5] Helicene	1.1003	[8] Helicene
6c	1.0942	[6] Helicene	1.0843	[8] Helicene
6d	1.0687	[7] Helicene	1.0762	[8] Helicene
6e	1.0789	[8] Helicene	-	-

a) For each compound included in this table, the $\Sigma F^{\bullet}_{r,s}$ of the photocyclisations leading to anthracenic structures (e.i. involving either one or two 8 positions) are lower than the highest value reported in the table.

b) Laarhoven and coll.[12).

atoms showing the largest $\Sigma F^{\bullet}_{r,s}$ values, as suggested by Scholtz et al.,[11] one would predict that the first cyclisation involves, in all cases but two, 5c and 6c, the more condensed aromatic systems. *If so*, only in the case of 5c would the induced asymmetric synthesis be determined by the second photocyclisation.

It should however be remembered that other factors can influence the regioselectivity[12,13] and that the photocyclodehydrogenations do not take place when the $\Sigma F^{\bullet}_{r,s}$ values are lower than unity;[14] exceptions to this last "rule" are however known in the [5] helicene series.[15]

CONCLUSION

The failure to observe asymmetric syntheses in the case of the higher benzologues of [10] helicene, raises a number of questions, for which we have no definite answers at the present time. It is thus clear that further experiments, including the use of irradiation bands of different wavelengths, should be undertaken.

EXPERIMENTAL

The IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer, the NMR spectra on a Jeol 100 MHz spectrograph (δ ppm from TMS) and the optical rotations (CHCl$_3$) on a Perkin-Elmer 141 polarimeter. A Carlo-Erba GI chromatograph was used for the GLC experiments (N$_2$ as carrier gas). Supports for column chromatography: alumina (neutral, Merck) or silica-gel (0·05–0·2 mm; Merck); solvents: Prolabo-RP "pur pour analyse".

I. *Synthesis of the bis(arylvinyl)arenes*

(a) *Synthesis of 1 and 3[3] and* (b) *synthesis of 5b-d and 6b-d.* These compounds are prepared according to Scheme 2. The intermediate 1,2-diarylethylenes and the bis(arylvinyl)arenes are synthesised by Wittig condensations. The m.p. (uncorrected) and analytical data are listed in Table 3 (1,2-diarylethylenes 12–15) and Table 4 (bis(arylvinyl)arenes 5b-d and 6b-d).

*Phosphonium salts.* Triphenylphosphine hydrobromide is prepared according to Surmatis et al.[16]

Equimolar amounts of this hydrobromide and of the required alcohol are dissolved in CHCl$_3$ and the solution is heated under reflux; the water produced is eliminated by azeotropic distillation, in the course of the reaction. DMF is added to the reaction

Table 3. Intermediate 1,2 - diarylethylenes 12–15

Compound	Yield %	Characterisation	m.p.
12	72	Recrystallised from cyclohexane	184–185°
13	65	Column chromatography on silicagel (eluent : ether)	140–142°
14	78	Recrystallised from D.M.F. Calcd for C$_{45}$H$_{34}$BrP Br : 11.67 Found : Br : 12.44%	180–183°
15	67	Precipitated from D.M.F. by dilution with ether Calcd for C$_{53}$H$_{38}$BrP Br = 10.2 Found Br : 9.97 %	230–233°

Table 4. Bis(arylvinyl)arenes 5b-d and 6b-d

Compound	Yield %	Elementary analyses	m.p.
5b	65	Calcd for C$_{34}$H$_{24}$ - C = 94.33 H = 5.60 Found C : 94.35 H = 5.74	214–216°
5c	60	Calcd for C$_{38}$H$_{26}$ C = 94.69 H = 5.44 Found C : 94.54 H = 5.40	245–247°
5d	76	Calcd for C$_{42}$H$_{28}$ C = 94.73 H = 5.31 Found C : 93.89 H = 5.26	215–217°
6b	70	Calcd for C$_{42}$H$_{28}$ C = 94.73 H = 5.31 Found C : 94.56 H = 5.53	195–197°
6c	72	Calcd for C$_{46}$H$_{30}$ C = 94.84 H = 5.20 Found C : 94.94 H = 5.26	201–203°
6d	75	Calcd for C$_{50}$H$_{22}$ C = 94.93 H = 5.10 Found C : 94.92 H = 5.20	141–143°

A. Moradpour *et al.*
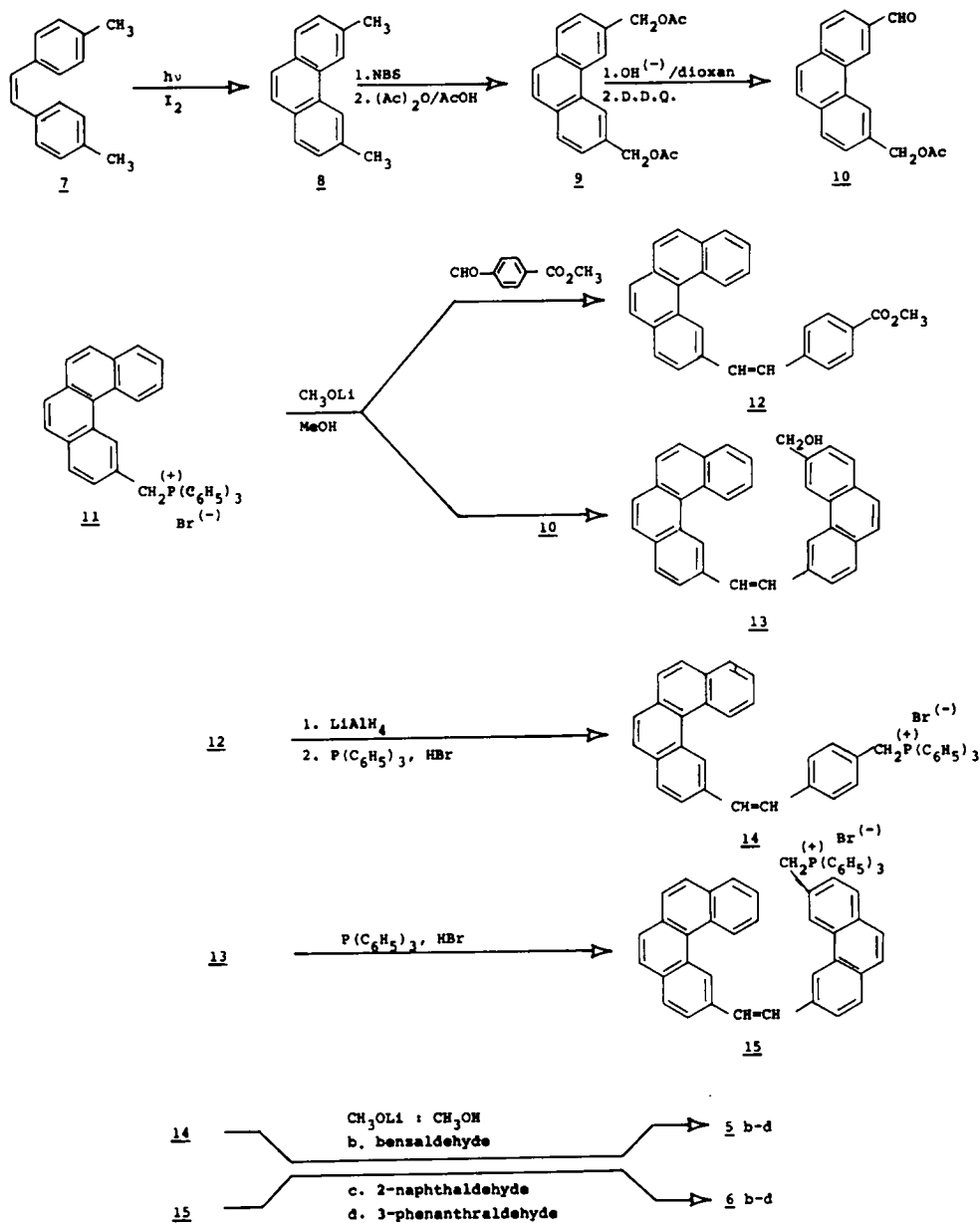
Scheme 2.

mixture and the chloroform is distilled. The phosphonium salt, which usually crystallises, is washed with anh. ether and dried.

Wittig condensation. Equimolar amounts of the phosphonium salt and of the required aldehyde, were dissolved in the minimum amount of dry MeOH and the mixture was refluxed under N_2; a slight excess (~10%) of a soln of MeOLi in MeOH (~1 N) was added dropwise. Refluxing was continued for 3 hr and the mixture stirred overnight, under N_2, at room temp. The ppt was filtered off and the mother liquor was diluted with an equal vol of H_2O. The crystals thus obtained were purified by column chromatography on alumina. The *cis/trans* mixtures were usually isomerised to the *trans* isomers ($C_6H_6 + I_2$; 3–4 hr reflux). However, when the next step of the photosynthesis was a photochemical ring-closure, the isomerisation was omitted.

3,6-diacetoxymethylphenanthrene 9. The diacetate was prepared by acetolysis of 3,6-dibromomethylphenanthrene[4b] (3·4 g; 0·02 mols) using NaOAc (3g) in AcOH (200 ml). The mixture was refluxed overnight, diluted with water and extracted with $CHCl_3$. The diester was purified by crystallisation from hexane, yield 2·2 g

(69%); m.p. 107–108° (hexane) (Calcd for $C_{20}H_{18}O_4$: C, 74·52; H, 5·63. Found: C, 74·2; H, 5·5%; NMR ($CDCl_3$) δ-CH_2 5·35 ppm, δ-CH_3 2·14 ppm).

6-Acetoxymethyl-3-formylphenanthrene 10. To a soln of 3,6 - diacetoxymethylphenanthrene (4·83 g; 0·015 mols) in 500 ml dioxan was added a soln of KOH (840 mg; 0·015 mols) in 25 ml H_2O and the mixture was stirred, at room temp (48 hr). The major part of the soln was evaporated, 200 ml H_2O were added and the soln was extracted with ether. The organic layer was concentrated, adsorbed on a column of silica-gel (400 g) and the products were eluted with ether: 2 g of unchanged diacetate was eluted first, followed by 1·76 g of the monoacetate-IR (neat) 2·94 μ (broad) and 5·8μ—3,6-dihydroxymethylphenanthrene (0·46 g) was eluted last. 1·36 g (0·0049 mols) of the monoacetate was oxidised with 1·1 g of DDQ.[17] 6 - Acetoxymethyl - 3 - formylphenanthrene was purified by column chromatography on silica-gel (ether), yield: 80%. IR (neat) 5·78 and 5·93 μ; NMR ($CDCl_3$) δ-CH_2 5·52 ppm; m.p. 73–74·5°.

1 - (2 - *Benzo[c]phenanthryl*) - 2 - (4 - *methoxycarbonyl-*

phenyl)ethylene 12. This compound was prepared from 11[2a] (3·3 g; 0·0057 mols) *and* 8 (0·939 g; 0·0057 *mols*).

1 - (2 - *Benzo[c]phenanthryl*) - 2 - (6 - *hydroxymethyl* - 3 - *phenanthryl)ethylene* 13. This product was synthesised by the condensation of 11 (2·3 g; 0·0039 mols) with 10 (1·08 g; 0·0039 mols).

1 - (2 - *Benzo[c]phenanthryl*) - 2 - (4 - *triphenylphosphoniomethylphenyl bromide)ethylene* 14. The salt 14 was prepared by reduction (LAH/ether) of ester 12 to the corresponding prim alcohol [NMR (CDCl₃/DMSO) 4·58 ppm] followed by treatment of this alcohol (620 mg; 0·0017 mols) with triphenylphosphine hydrobromide (600 mg; 0·0018 mols).

1 - (2 - *Benzo[c]phenanthryl*) - 2 - (3 - (6 - *triphenylphosphoniomethyl* - 3 - *phenanthryl bromide)ethylene* 15. The alcohol 13 (NMR CDCl₃/DMSO δ_{CH_2} 5·0 ppm; 1·9 g; 0·0024 mols) was converted to 15 by treatment with triphenylphosphine hydrobromide (0·825 g; 0·0024 mols).

Photochemical ring-closures. The apparatus used for the photochemical ring-closures with circularly polarized light has already been described.[18] The samples were photolysed in benzene soln in the presence of a trace of I₂ (Pyrex flask: 660 ml) using a 290–270 nm irradiation band, circularly polarized at 313 nm. In the case of 5a-c and 6a, aliquots from the mixture were analysed, from time to time, by GLC (column: 0·8 m; 2 mm diam., packed with 4% OV₁ on gas chrom Q 60–80 mesh; Temp ranges from 250 to 335°; carrier flow 70 ml min⁻¹).

For the higher benzologues 5d-e and 6b-e, TLC (alumina/Hexane + 4% EtOAc) were used to detect the end of the reaction. The helicenes were isolated and purified by column chromatography (alumina/hexane + 4% ethyl acetate) and characterised by GLC, using authentic samples for comparison. The optical rotations were measured in CHCl₃.

REFERENCES

[1a]A. Moradpour, G. Balavoine, J. F. Nicoud, H. Kagan and G. Tsoucaris, *J. Am. Chem. Soc.* 93, 2353 (1971); [b]H. Kagan, A. Moradpour, G. Balavoine, J. F. Nicoud, R. H. Martin and J. P. Cosyn, *Tetrahedron Letters* 2479 (1971).

[2a]W. J. Bernstein, M. Calvin and O. Buchardt, *J. Am. Chem. Soc.* 94, 494 (1972); [b]W. J. Bernstein, M. Calvin and O. Buchardt, *Tetrahedron Letters* 2195 (1972).

[3]R. H. Martin, M. J. Marchant and M. Baes, *Helv. Chim. Acta* 54, 358 (1971).

[4a]R. H. Martin, G. Morren and J. J. Schurter, *Tetrahedron Letters* 3683 (1969); [b]R. H. Martin and M. Baes, *Tetrahedron.*

[5]G. J. Hammond, S. C. Shim and S. P. Van, *Mol. Photochem.* 1, 89 (1969).

[6]J. Klueger, G. Fischer, Ch. Goedicke and H. Stegemeyer, *Chem. Phys. Letters* 8, 279 (1971).

[7]M. S. Newman and D. Lednicer, *J. Am. Chem. Soc.* 78, 4765 (1965).

[8]R. H. Martin and M. J. Marchant, *Tetrahedron* 30, 343 (1974).

[9]V. Libert (Brussels), unpublished results.

[10]Ch. Goedicke and H. Stegemeyer, *Tetrahedron Letters* 937 (1970).

[11]M. Scholz, M. Muhlstadt and F. Dietz, *Ibid.* 665 (1967).

[12]W. H. Laarhoven, Th. J. H. M. Cuppen and R. J. F. Nivard, *Tetrahedron* 26, 4865 (1970).

[13]T. Wismonski-Knittel, T. Bercovici and E. Fischer, *J. Chem. Soc. Chem. Comm.* 716 (1974).

[14]W. H. Laarhoven, Th. J. H. M. Cupper and R. J. F. Nivard, *Rec. Trav. Chim. Pays-Bas* 87, 687 (1968).

[15]H. A. H. Tinnemans and W. H. Laarhoven, *J. Am. Chem. Soc.* 96, 4617 (1974); footnote (13) p. 4619.

[16a]J. D. Surmatis and A. Ofner, *J. Org. Chem.* 28, 2735 (1963); [b]H. Freyschlag, H. Grassner, A. Nurrenbach, H. Pommer, W. Reif and W. Sarnecki, *Angew. Chem. Int. Edit.* 4, 287 (1965).

[17]L. F. Fieser and M. Fieser, *Reagents for Organic Synthesis*, Vol. 1, p. 217. Wiley, New York (1967).

[18]G. Balavoine, A. Moradpour and H. B. Kagan, *J. Am. Chem. Soc.* 96, 5152 (1974).