Reaction of Aryl Aldehydes with Thiocyanates in the Presence of Tributylphosphine

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Aryl aldehydes react with methyl thiocyanate in the presence of tributylphosphine to afford *S*-methyl thiobenzoates and arylacetonitriles in good yields. This is a novel disproportionation reaction involving carbon–carbon bond formation. These compounds thus obtained are easily converted into deoxybenzoins using sodium hydride. On the other hand, *p*-dialkylaminobenzaldehydes react with methyl thiocyanate under the same conditions to furnish both the corresponding *trans*-dicyanostilbenes and succinonitriles in moderate yields. Finally, the reaction was carried out with aryl thiocyanates resulting in the formation of addition products.

In our study directed toward the synthesis of very strained heterocycles, it became necessary to obtain (α-methylthio)phenylacetonitrile. In order to prepare it directly from benzaldehyde, we intended to exploit a convenient procedure such as the reaction of benzaldehyde with methyl thiocyanate in the presence of tributylphosphine. A hitherto reported conversion of benzaldehyde into (α-methylthio)phenylacetonitrile has required hazardous reagents and multistep procedures.[1]

From the experiment mentioned above, we found a novel disproportionation reaction involving carbon–carbon bond formation. That is, benzaldehyde reacted with methyl thiocyanate in the presence of tributylphosphine to give both *S*-methyl thiobenzoate and phenylacetonitrile.[2] On the other hand, in the case of *p*-halogenobenzaldehydes and *p*-trifluoromethylbenzaldehyde, the corresponding oxirane derivatives were isolated and, in the case of *p*-dialkylaminobenzaldehydes, the corresponding *trans*-dicyanostilbene and succinonitrile derivatives were obtained. Finally, the reaction of benzaldehyde with phenyl thiocyanate under the same conditions afforded an expected product, (α-phenylthio)phenylacetonitrile.

Results and Discussion

Reaction of Aryl Aldehydes with Methyl Thiocyanate.—The reaction of aryl aldehydes (**1**) with methyl thiocyanate (**2**) was carried out in the presence of tributylphosphine. The compounds thus obtained were found to be *S*-methyl thiobenzoates and arylacetonitriles. Our results are summarized in Table 1.

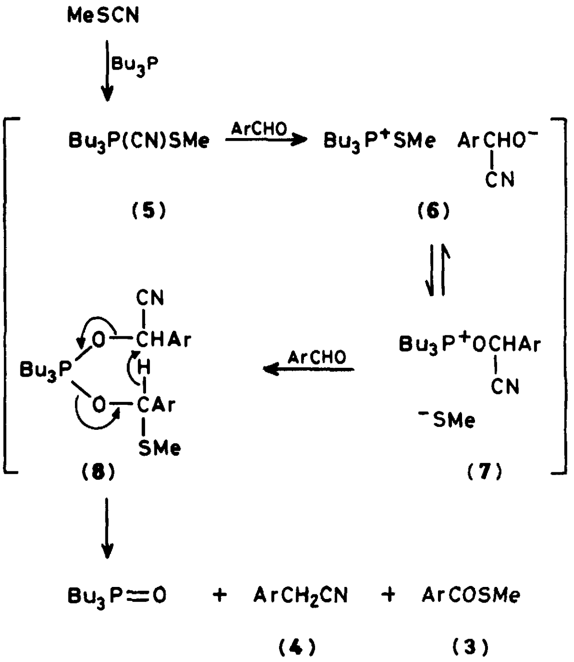
Table 1.

$$\underset{(1)}{2\,\mathrm{ArCHO}} + \underset{(2)}{\mathrm{MeSCN}} \xrightarrow{\mathrm{Bu_3P}} \underset{(3)}{\mathrm{ArCOSMe}} + \underset{(4)}{\mathrm{ArCH_2CN}}$$

		Yield (%)		
Entry	Aldehyde (**1**)	(**3**)	(**4**)	Total
a	Benzaldehyde	47	35	82
b	*p*-Tolualdehyde	47	45	92
c	*p*-Anisaldehyde	16	31	47
d	*p*-Nitrobenzaldehyde	22	*a*	22
e	α-Naphthalene-1-carbaldehyde	15	32	47

[a] Not isolated.

This unprecedented reaction is considered to proceed *via* the route shown in Scheme 1.†



Scheme 1.

Methyl thiocyanate is initially activated by tributylphosphine to generate a complex (**5**), which in turn attacks an aryl aldehyde to form a key intermediate (**7**), in equilibrium with (**6**). This species (**7**) then reacts with another molecule of aldehyde to give (**8**). The intermediate (**8**) is immediately converted into (**3**) and (**4**) with the elimination of tributylphosphine oxide.

It is interesting to note that *p*-chlorobenzaldehyde reacted with methyl thiocyanate under the same conditions as mentioned above to give 2,3-bis-(*p*-chlorophenyl)-2-cyano-oxirane (**9a**) instead of expected disproportionation products. In a similar way, *p*-bromobenzaldehyde and *p*-trifluoromethylbenzaldehyde were converted into the corresponding oxiranes (**9b** and **c**). The reaction seems to proceed *via* an α-methylthio-(*p*-substituted phenyl)acetonitrile as an intermediate. This is

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† We thank the referee for his suggestions concerning the mechanism.

perhaps because the electron-withdrawing substituents inhibit such hydride-transfer processes as mentioned for the disproportionation reaction. Table 2 summarizes our results.

On the other hand, *p*-dialkylaminobenzaldehydes showed a different behaviour. That is, the corresponding *trans*-dicyanostilbene (**10**) and succinonitrile (**11**) derivatives were obtained in moderate yields. The results are summarized in Table 3.

The formation of compounds (**10**) and (**11**) may be explained by Scheme 2.

An intermediate, (**14**), generated from tributylphosphine and methyl thiocyanate, reacts with an aryl aldehyde to give an intermediate (**16**) *via* (**15**). The intermediate (**16**) reacts with tributylphosphine rapidly to form a key species (**17**), which then attacks (**16**) to give the succinonitrile (**11**); alternatively, (**17**) is changed competitively into a stable carbene (**18**).[3] The dimerization of (**18**) results in the formation of the stilbene (**10**). This fact may be explained by the hypothesis that an aldehyde bearing a dialkylamino group does not act as a hydride acceptor owing to the strong electron-donating effect of the R_2N group.

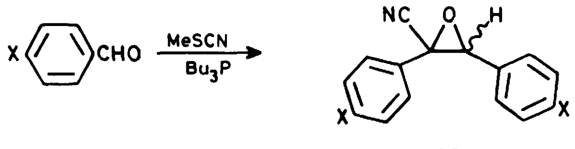
Some methods have been reported for the synthesis of *trans*-dicyanostilbene derivatives.[4] Compared with these procedures, the present method is more simple to use. That is, the *trans*-dicyanostilbene derivatives can be easily prepared and purified by the usual work-up using column chromatography.

It is interesting to note that (*p*-dimethylamino)dicyanostilbene shows thermochromism. The colour of a chloroform solution of *trans*-dicyanostilbene changed from red to yellow on heating. With decreasing temperature, the colour returned to red and then removal of the solvent gave the starting *trans*-dicyanostilbene.

Photolysis of trans-*Bis*-(p-*dimethylamino*)-α,β-*dicyanostilbene.*—When a solution of *trans*-bis-(*p*-dimethylamino)-dicyanostilbene in chloroform was photolysed by irradiation with a high-pressure mercury lamp, a *cis–trans* isomerization occurred to give an equilibrium mixture of *cis*:*trans* ratio 2:5. On the other hand, when this reaction was conducted in the presence of oxygen for 30 min, the expected 3,6-bis(dimethylamino)-9,10-dicyanophenanthrene (**20**) was isolated in 17% yield.[5]

Hydrogenation of trans-*Bis*-(p-*diethylamino*)-α,β-*dicyanostilbene* (**10b**).—Toda and Kanno[6] reported that sodium borohydride was an effective reagent for the reduction of α,β-un-

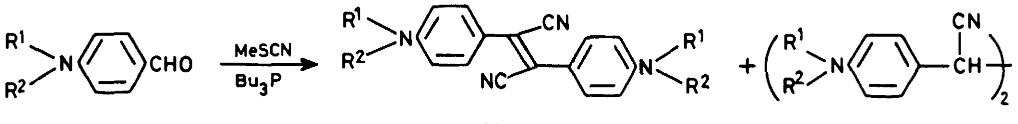
Table 2.



(9)

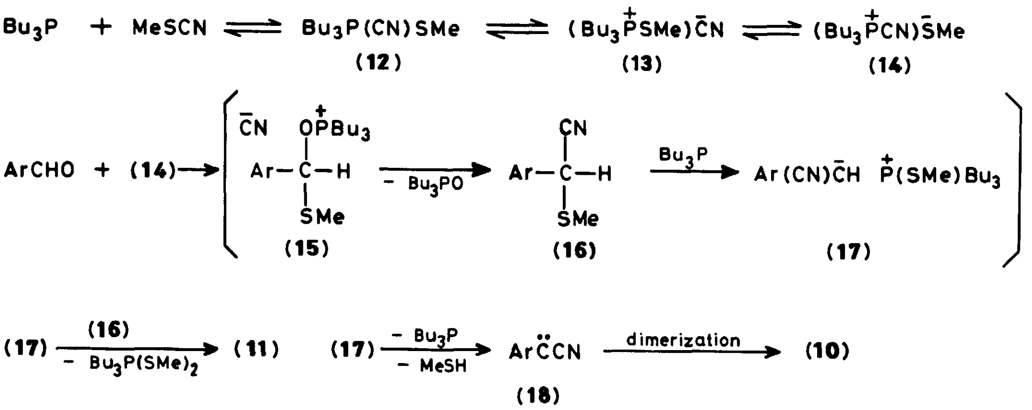
	X	Yield (%)
(**9a**)	Cl	55
(**9b**)	Br	15
(**9c**)	CF_3	22

Table 3.

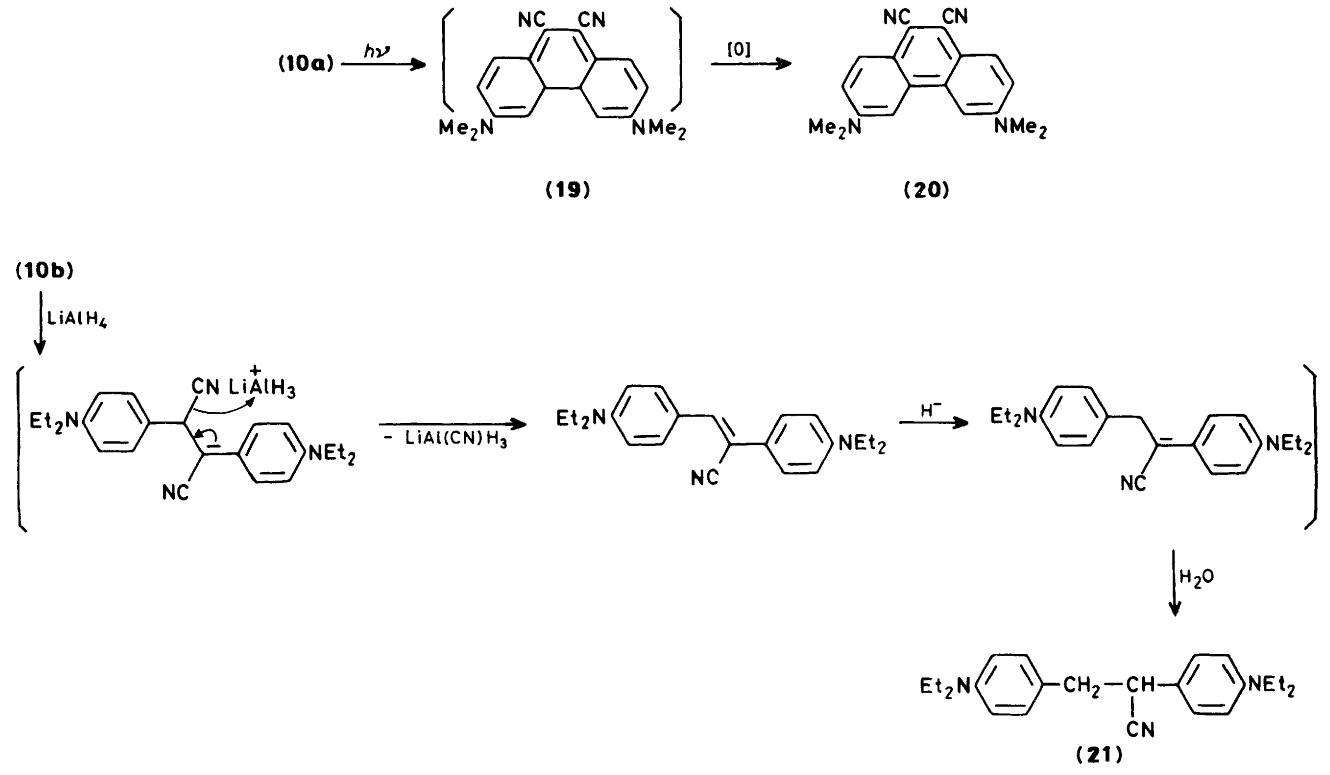


(10) **(11)**

Entry	R¹	R²	Yield (%) (10)	Yield (%) (11)	Yield (%) Total
a	Me	Me	48	15	63
b	Et	Et	22	41	63
c	Me	Bu	49	31	80
d	Me	Et	17	35	52
e	Et	Ph	44	35	79

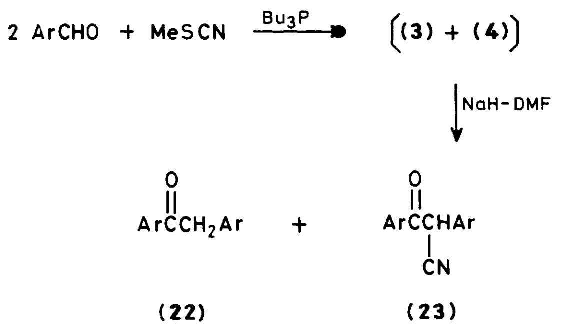


Scheme 2.



Scheme 3.

Table 4.



Entry	Aryl aldehyde	Yield (%) (22)	(23)	Total
a	Benzaldehyde	61	5	66
b	*p*-Tolualdehyde	45	24	69
c	*m*-Tolualdehyde	40		40
d	*p*-Anisaldehyde	38		38
e	*p*-Nitrobenzaldehyde	28		28
f	Piperonal		31	31

saturated nitriles. However, in the case of *trans*-bis-(*p*-diethylamino)-α,β-dicyanostilbene (**10b**), reduction did not occur with sodium borohydride or Pd–C-catalysed hydrogenation. The use of lithium aluminium hydride in tetrahydrofuran (THF) reduced (**10**) to give the unexpected 2,3-bis-(*p*-diethylaminophenyl)propionitrile (**21**) *via* loss of a cyano group, in 84% yield (Scheme 3).

Conversion of Aryl Aldehydes into Deoxybenzoins.—Pursuing the synthetic utility of the present reaction, we intended to synthesize cyanodeoxybenzoins (**23**) directly from aryl aldehydes by condensation of the precursors (**3**) and (**4**) using sodium hydride in *N*,*N*-dimethylformanide (DMF). However, the results showed that unexpected products, deoxybenzoins (**22**) were isolated as major products along with minor amounts of (**23**).[7] Our results are shown in Table 4.

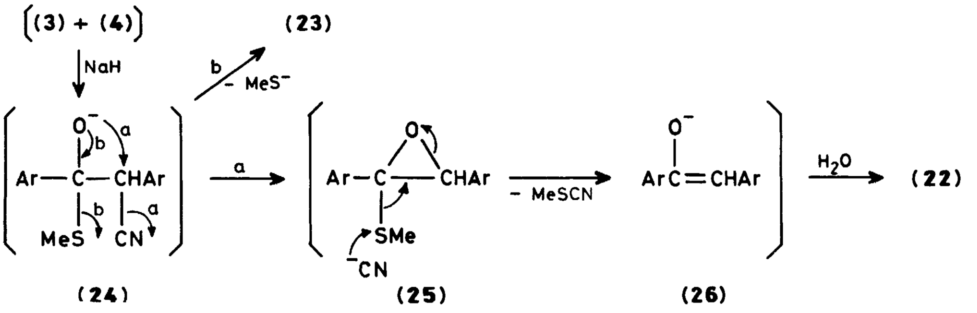
It was also found that the yields of (**22**) and (**23**) were fairly dependent on the reaction temperature. In the exceptional case of piperonal, only the nitrile (**23**) was obtained. The reaction can be explained by assuming a key intermediate (**24**), which is derived from the condensation of (3) and (4) using sodium hydride. Compound (**22**) is formed from (**24**) through intermediates (**25**) and (**26**) with the elimination of methyl thiocyanate (path a), while (**24**) can also lose a methylthio anion to give (**23**), an expected condensation product (path b) (see Scheme 4).

Many methods to synthesize deoxybenzoins have appeared in the literature,[8] but the present procedure provides a convenient method to prepare deoxybenzoins directly from aryl aldehydes. It is also noteworthy that coupled use of sodium hydride and copper(I) iodide in the present reaction resulted in the formation of dibenzoylphenylmethane. Use of copper(I) iodide seems to activate species (**26**).

Reaction of Aryl Aldehydes with Aryl Thiocyanates.—The present reaction was carried out with aryl thiocyanates (**27**) in place of methyl thiocyanate. The products were found to be addition compounds, α-arylthio(phenyl)acetonitriles (**28**). This reaction is similar to that of aryl selenocyanates.[9] The results are shown in Table 5.

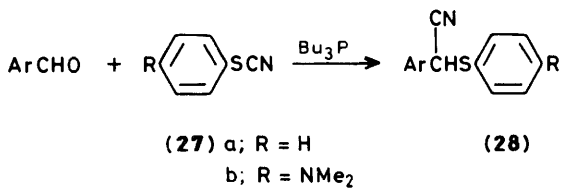
A difference in this reaction between that of methyl thiocyanate is explained by the electronic effect; that is, an intermediate corresponding to (6) cannot undergo hydride transfer, owing to the electron-withdrawing effect of the aryl group.

In analogy with methyl thiocyanate, benzyl thiocyanate[10] converted benzaldehyde into both *S*-benzyl thiobenzoate[11] and



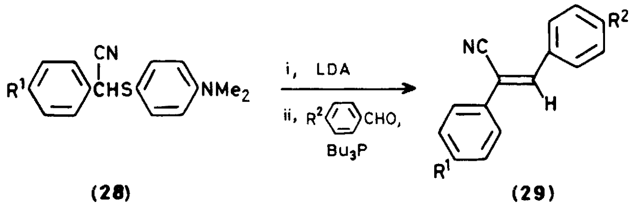
Scheme 4.

Table 5.



Entry	Aldehyde	Compound (27)	Yield of (28) (%)
a	*p*-Tolualdehyde	**(27a)**	81
b		**(27b)**	84
c	*p*-Anisaldehyde	**(27a)**	60
d		**(27b)**	81
e	Piperonal	**(27b)**	94

Table 6.



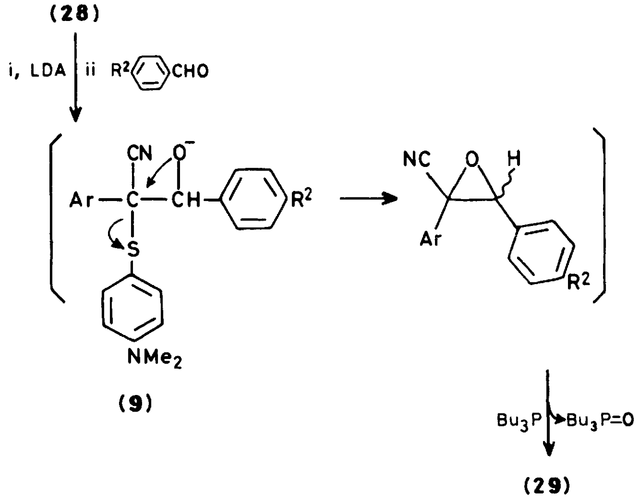
Entry	R^1 in (**28**)	R^2 in aryl aldehyde	Yield of (**29**) (%)
a	Me	H	52
b	Me	Me	35
c	Me	MeO	34
d	MeO	H	38
e	MeO	Me	32
f	MeO	MeO	53

phenylacetonitrile in 25 and 48% yield, respectively. In the case of mesityl thiocyanate,[11] both disproportionation and addition reactions took place.

The following substituted compounds could not undergo this reaction: *p*-chloro- and *p*-nitro-phenyl thiocyanates as aryl thiocyanates, ketones and aliphatic aldehydes as carbonyl compounds, and triphenylphosphine and trimethyl phosphite as phosphorus compounds.

Conversion of Compounds (**28**) *into* (Z)-*Cyanostilbenes*.—Compounds (**28**) were treated with lithium di-isopropylamide (LDA), followed by addition of aryl aldehydes and tributylphosphine, to furnish (*Z*)-cyanostilbenes (**29**) in moderate yields. The results are summarized in Table 6.

The reaction is considered to proceed as shown in Scheme 5.



Scheme 5.

Experimental

Microanalyses were performed with a Perkin-Elmer 240 elemental analyser at the Analytical Center of Chiba University. I.r., u.v., mass, and ^1H n.m.r. spectra were measured with Japan Spectroscopic Co. DS 403G, Hitachi EPS-3T, Hitachi RMU 6MC, and Japan Electron Optics Lab. Co. C-60 HL and FX-100 instruments, respectively. Silica gel used in column chromatography was Wakogel C-200, and silica gel used for t.l.c. was Wako gel B-5F. Ether is diethyl ether.

General Procedure for Preparation of S-*Methyl Thiobenzoates* (**3**) *and Aryl Acetonitriles* (**4**).—To an ice-cold mixture of benzaldehyde (212 mg, 2 mmol) and tributylphosphine (0.27 ml, 1.1 mmol) was added methyl thiocyanate (0.073 ml, 1 ml) dropwise with a syringe, under argon. After the addition was complete, the mixture was stirred for 1 h at 0 °C and for an additional 2 h at ambient temperature. The reaction mixture was worked up by preparative t.l.c. on silica gel using a 2:1 mixture of benzene and hexane as eluant to afford compounds (**3a**) and (**4a**) in 47 and 35% yield, respectively. Compounds thus obtained were confirmed by n.m.r. and i.r. spectral comparison of authentic samples: (**3a**),[12] (**3b**),[13] (**3c**),[14] (**3d**),[15] (**3e**),[14] (**4a**),[16] (**4b**),[17] (**4c**),[18] and (**4e**).[19]

2,3-*Bis*-(p-*chlorophenyl*)-2-*cyano-oxirane* (**9a**), 2,3-*Bis*-(p-*bromophenyl*)-2-*cyano-oxirane* (**9b**), *and* 2,3-*Bis*-(p-*trifluoromethyl*)-2-*cyano-oxirane* (**9c**).—*p*-Chlorobenzaldehyde, *p*-bromobenzaldehyde, and (*p*-trifluoromethyl)benzaldehyde reacted with methyl thiocyanate under the same conditions as mentioned above to give the oxiranes (**9**) as isolated products; (**9a**): *white prisms*, m.p. 119—120 °C (from ethanol); $\delta_H(CDCl_3)$

7.48 (8 H, m) and 4.15 (1 H, s); *m/z* 289 (M^+), 254, 149, and 114; $\nu_{max.}$(KBr) 2 240w, 1 600w, 1 495s, 1 400m, 1 095s 1 020m, 840s, and 810s cm^{-1} (Found: C, 61.95; H, 3.2; N, 4.75. $C_{15}H_9Cl_2NO$ requires C, 62.10; H, 3.13; N, 4.83%).

(9b): *white needles*, m.p. 137 °C (from hexane); δ_H(CDCl$_3$) 7.53 (8 H, m) and 4.07 (1 H, s); *m/z* 379 (M^+), 298, 219, 114, and 89; $\nu_{max.}$(KBr) 2 250w, 1 595m, 1 495s, 1 400m, 1 260w, 1 080s, 1 010s, 840s, and 810s cm^{-1} (Found: C, 47.6; H, 2.5; N, 3.7. $C_{15}H_9Br_2NO$ requires C, 47.53; H, 2.66; N, 3.70%).

(9c): *white prisms*, m.p. 108—109 °C (from hexane); δ_H(CDCl$_3$) 7.77 (8 H, m) and 4.07 (1 H, s); *m/z* 357 (M^+), 183, 175, 145, and 102; $\nu_{max.}$(KBr) 2 260w, 1 330s, 1 260m, 1 080s, 1 025m, 860m, and 830m cm^{-1} (Found: C, 57.3; H, 2.6; N, 3.9. $C_{17}H_9F_6NO$ requires C, 57.15; H, 2.54; N, 3.92%).

trans-*Bis*-(p-*dimethylamino*)-α,β-*dicyanostilbene* **(10a)** *and* 2,3-*Bis*-(p-*dimethylaminophenyl*)*succinonitrile* **(11a)**.—The reaction was carried out by the same procedure as described in the preparation of compounds (3) and (4). The reaction mixture was worked up by column chromatography on silica gel using chloroform as eluant to furnish compounds **(10a)** and **(11a)**; **(10a)**: *red needles*, m.p. 296—297 °C (from ether); δ_H(CDCl$_3$) 7.74 (4 H, m), 6.72 (4 H, m), and 3.06 (12 H, s); *m/z* 316 (M^+) and 157; $\nu_{max.}$(KBr) 2 880w, 2 200s, 1 595s, 1 520s, 1 365s, 1 195s, and 820s cm^{-1} (Found: C, 75.9; H, 6.4; N, 17.85. $C_{20}H_{20}N_4$ requires C, 75.92; H, 6.37; N, 17.71%).

(11a): *yellow needles*, m.p. 189—190 °C (from hexane); δ_H(CDCl$_3$) 6.99 (8 H, m), 4.33 (2 H, s), 3.02 (6 H, s), and 2.99 (6 H, s); *m/z* 318 (M^+), 316, 184, and 154; $\nu_{max.}$(KBr) 2 880m, 2 250w, 1 610s, 1 530s, 1 370m, 1 180m, and 810m cm^{-1} (Found: C, 75.3; H, 6.8; N, 17.5. $C_{20}H_{22}N_4$ requires C, 75.44; H, 6.96; N, 17.50%).

The following compounds were similarly obtained by the above method. **(10b)**: *red prisms*, m.p. 191—192 °C (from ether); δ_H(CDCl$_3$) 7.68 (4 H, d, *J* 9 Hz), 6.63 (4 H, d, *J* 9 Hz), 3.37 (8 H, q, *J* 7 Hz), and 1.20 (12 H, t, *J* 7 Hz); *m/z* 372 (M^+), 357, 313, and 186; $\nu_{max.}$(KBr) 2 950m, 2 200m, 1 590s, 1 520m, 1 270s, 1 195s, 1 160s, and 824s cm^{-1} (Found: C, 77.6; H, 7.6; N, 15.1. $C_{24}H_{28}N_4$ requires C, 77.38; H, 7.58; N, 15.04%).

(10c): *red prisms*, m.p. 106—108 °C (from ether); δ_H(CDCl$_3$) 7.12 (4 H, m), 6.63 (4 H, m), 3.20 (4 H, t, *J* 7 Hz), 2.85 (6 H, s), 1.40 (8 H, m), and 0.97 (6 H, t, *J* 7 Hz); *m/z* 400 (M^+) and 357; $\nu_{max.}$(KBr) 2 940m, 2210m, 1 605s, 1 530m, 1 395m, 1 200s, and 829m cm^{-1} (Found: C, 78.0; H, 8.0; N, 14.0. $C_{26}H_{32}N_4$ requires C, 77.96; H, 8.05; N, 13.99%).

(10d): *red prisms*, m.p. 186 °C (from ether); δ_H(CDCl$_3$) 7.80 (4 H, d, *J* 8 Hz), 6.75 (4 H, d, *J* 8 Hz), 3.52 (4 H, q, *J* 7 Hz), 3.00 (6 H, s), and 1.12 (6 H, t, *J* 7 Hz); *m/z* 344 (M^+), 329, 299, and 158; $\nu_{max.}$(KBr) 2 950m, 2 210m, 1 600s, 1 525m, 1 390m, 1 275m, 1 200s, and 830m cm^{-1} (Found: C, 76.8; H, 7.0; N, 16.3. $C_{22}H_{28}N_4$ requires C, 76.71; H, 7.02; N, 16.29%).

(10e): *red prisms*, m.p. 144—146 °C (from hexane); δ_H(CDCl$_3$) 7.68 (4 H, d, *J* 9 Hz), 7.30 (10 H, m), 6.75 (4 H, d, *J* 9 Hz), 3.80 (4 H, d, *J* 9 Hz), and 1.23 (6 H, t, *J* 7 Hz); *m/z* 468 (M^+), 453, and 219; $\nu_{max.}$(KBr) 2 926m, 2 910s, 2 210s, 1 600s, 1 510s, and 830 s cm^{-1} (Found: C, 81.8; H, 6.1; N, 11.9. $C_{32}H_{28}N_4$ requires C, 82.02; H, 6.02; N, 11.96%).

(11b): *red prisms*, m.p. 186 °C (from ether); δ_H(CDCl$_3$) 7.08 (4 H, d, *J* 9 Hz), 6.61 (4 H, d, *J* 9 Hz), 4.04 (2 H, s), 3.35 (8 H, q, *J* 7 Hz), and 1.16 (12 H, t, *J* 7 Hz); *m/z* 375 (M^+), 372, 357, 187, and 172; $\nu_{max.}$(KBr) 2 950m, 2 240w, 1 610s, 1 520s, 1 360m, 1 270m, 1 200m, and 819m cm^{-1} (Found: C, 76.9; H, 8.1; N, 14.9. $C_{20}H_{22}N_4$ requires C, 76.96; H, 8.07; N, 14.95%).

(11c): *white needles*, m.p. 187 °C (from ether); δ_H(CDCl$_3$) 7.08 (4 H, m), 6.62 (4 H, m), 4.05 (2 H, s), 3.31 (4 H, t, *J* 7 Hz), 2.90 (6 H, s), 1.40 (8 H, m), and 0.95 (6 H, m); *m/z* 402 (M^+), 400, 375, and 332; $\nu_{max.}$(KBr) 2 290m, 2 900m, 2 240m, 1 615s, 1 530s, 1 375m, 1 185m, and 810s cm^{-1} (Found: C, 77.5; H, 8.5; N, 13.8. $C_{26}H_{34}N_4$ requires C, 77.57; H, 8.51; N, 13.92%).

(11d): *yellow needles*, m.p. 174—175 °C (from ether); δ_H(CDCl$_3$) 7.08 (4 H, d, *J* 9 Hz), 6.49 (4 H, d, *J* 9 Hz), 4.06 (2 H, s), 3.41 (4 H, q, *J* 7 Hz), 2.92 (6 H, s), and 1.13 (6 H, t, *J* 7 Hz); *m/z* 346 (M^+), 329, and 173; $\nu_{max.}$(KBr) 2 950w, 2 240w, 1 605s, 1 520s, 1 380m, 1 350w, 1 200w, 1 160w, and 820m cm^{-1} (Found: C, 76.2; H, 7.6; N, 16.2. $C_{22}H_{26}N_4$ requires C, 76.27; H, 7.56; N, 16.17%).

(11e): *yellow prisms*, m.p. 153—154 °C (from ether); δ_H(CDCl$_3$) 7.33 (4 H, d, *J* 9 Hz), 7.12 (10 H, m), 6.81 (4 H, d, *J* 9 Hz), 4.08 (2 H, s), 3.77 (4 H, q, *J* 7 Hz), and 1.22 (6 H, t, *J* 7 Hz); *m/z* 470 (M^+), 235, and 221; $\nu_{max.}$(KBr) 2 960m, 2 240w, 1 610m, 1 590m, 1 510s, and 1 495s cm^{-1} (Found: C, 81.5; H, 6.4; N, 11.8. $C_{32}H_{30}N_4$ requires C, 81.67; H, 6.43; N, 11.82%).

3,6-*Bis*(*dimethylamino*)-9,10-*dicyanophenanthrene* **(20)**.—A solution of compound **(10a)** in chloroform was irradiated, in a vessel open to the air, with a high-pressure mercury lamp (Toshiba H 400-P) for 0.5 h surrounded by a Pyrex cooling jacket. Usual work-up of the reaction mixture furnished compound **(20)** as yellow prisms, m.p. 252 °C (from chloroform); δ_H(CDCl$_3$) 8.05 (2 H, d, *J* 9 Hz), 7.45 (2 H, s), 7.20 (2 H, d, *J* 9 Hz), and 3.22 (12 H, s); *m/z* 314 (M^+), 299, 156, and 134; $\nu_{max.}$(KBr) 2 900m, 2 210s, 1 615s, 1 380s, 1 190m, 830s, and 810s cm^{-1}.

2,3-*Bis*-(p-*diethylaminophenyl*)*propionitrile* **(21)**.—Compound **(10b)** was treated with lithium aluminium hydride in THF at 0 °C for 0.5 h. The reaction mixture was quenched with water and extracted with benzene. The extract was worked up by preparative t.l.c. on silica gel using benzene as eluant to afford compound **(21)** as yellow needles (from hexane) in 84% yield, δ_H(CDCl$_3$) 7.01—6.47 (8 H, m), 3.37 (8 H, q, *J* 7 Hz), 3.70—2.90 (3 H, m), and 1.17 (12 H, t, *J* 7 Hz); *m/z* 349 (M^+), 187, 162, 161, and 118; $\nu_{max.}$(KBr) 2 950s, 2 900s, 2 230m, 1 610s, 1 520s, 1 360m, 1 270m, 1 200m, and 820m cm^{-1}.

General Procedure for Preparation of Deoxybenzoins **(22)** *and Cyanodeoxybenzoins* **(23)**.—To an ice-cold mixture of benzaldehyde (212 mg, 2 mmol) and tributylphosphine (0.27 ml, 1.1 mmol) was added methyl thiocyanate (0.073 ml, 1 mmol) dropwise with a syringe under argon. After the addition was complete, the mixture was stirred for 1 h at 0 °C and for an additional 2 h at ambient temperature. To the reaction mixture was added sodium hydride (50% dispersion in oil; 50 mg, 1 mmol) in DMF (2 ml). The resulting solution was stirred for 2 h at room temperature, quenched with dil. HCl, and extracted with chloroform. The extract was concentrated and then worked up by preparative t.l.c. upon silica gel using a 4:1 mixture of benzene–hexane as eluant to give compound **(22a)**[20] and **(23a)**[21] in 60 and 5% yield, respectively.

Compounds **(22b)**,[22] **(22c)**, **(22d)**,[23] **(22e)**, **(23b)**, and **(23f)** were prepared in a similar way.

(22c): oil, δ_H(CCl$_4$) 7.63 (4 H, m), 6.95 (4 H, m), 3.98 (2 H, s), and 2.71 (6 H, s); $\nu_{max.}$(KBr) 2 900m, 1 680s, and 1 600m cm^{-1}.

(22e): oil, δ_H(CDCl$_3$) 8.50 (4 H, m), 7.75 (2 H, m), and 4.80 (2 H, s); $\nu_{max.}$(KBr) 3 060m, 2 910w, 1 700s, 1 600m, 1 520s, 1 350s, and 1 210m cm^{-1}.

(23b): oil, δ_H(CCl$_4$) 7.8 (2 H, d, *J* 8 Hz), 7.17 (6 H, m), 5.35 (1 H, s), 2.34 (3 H, s), and 2.30 (3 H, s); $\nu_{max.}$(KBr) 3 015m, 2 900s, and 2 250m cm^{-1}.

(23f): oil, δ_H(CCl$_4$) 7.47 (2 H, m), 6.83 (4 H, m), 6.03 (2 H, s), 5.97 (2 H, s), and 5.47 (1 H, s); $\nu_{max.}$(KBr) 2 890s, 2 250m, 1 680s, and 1 600s cm^{-1}

Formation of Dibenzoylphenylmethane.—The coupled use of sodium hydride (1 mmol) and copper(I) iodide (1 mmol) under the same conditions as described in the preparation of (**22**) and (**23**) resulted in the formation of dibenzoylphenylmethane[24] in 37% yield.

Preparation of Aryl Thiocyanates (**27**).—*Compound* (**27a**). Aniline (18.6 g) was dissolved in a mixture of conc. H_2SO_4 (40 ml) and water (160 ml) in a 1 l beaker. To the well stirred mixture was added a solution of sodium nitrite (18.7 g) in water (100 ml) dropwise at below 10 °C. The aqueous solution of the diazonium salt thus obtained was added drop by drop to a solution of KSCN (38.8 g) and $FeCl_3$ (30 g) in water (50 ml) at ambient temperature. After the addition was complete, the mixture was stirred overnight and then distilled (steam) to give a yellow solution which was then extracted with benzene. The extract was evaporated and the residue worked up by column chromatography on silica gel using a 1:1 mixture of benzene–hexane as eluant. The second coloured fraction was collected and distilled under reduced pressure to give the phenylthiocyanate (**27a**) as an oil, b.p. 61—62 °C/3 Torr, in 60% yield.

Compounds (**27b**),[25] *p*-chlorophenyl thiocyanate,[26] and *p*-nitrophenyl thiocyanate[27] were prepared according to the literature methods.

(α-*Arylthio*)*phenylacetonitriles* (**28**).—The reaction was carried out with an aryl thiocyanate in place of methyl thiocyanate by the same procedure as described in the preparation of compounds (**3**) and (**4**); the following compounds were prepared.

(**28a**): *white prisms*, m.p. 82—83 °C (from EtOH); $\delta_H(CDCl_3)$ 7.4 (5 H, s), 7.2 (4 H, s), 4.8 (1 H, s), and 2.4 (3 H, s); *m/z* 239 (M^+); $\nu_{max.}$(KBr) 3 050m, 2 920s, and 2 230w cm^{-1} (Found: C, 75.25; H, 5.5; N, 5.8. $C_{15}H_{13}NS$ requires C, 75.28; H, 5.47; N, 5.85%).

(**28b**): *yellow plates*, m.p. 120—121 °C (from EtOH); $\delta_H(CDCl_3)$ 7.4 (2 H, d, *J* 10 Hz), 7.25 (4 H, s), 6.7 (2 H, d, *J* 10 Hz), 4.8 (1 H, s), 3.05 (6 H, s), and 2.4 (3 H, s); *m/z* 282 (M^+); $\nu_{max.}$ (KBr) 3 050w, 2 850s, and 2 300w cm^{-1} (Found: C, 72.3; H, 6.4; N, 9.9. $C_{17}H_{18}N_2S$ requires C, 72.30; H, 6.42; N, 9.92%).

(**28**): *white prisms*, m.p. 69—70 °C (from EtOH); $\delta_H(CDCl_3)$ 7.4 (5 H, s), 7.25 (2 H, d, *J* 10 Hz), 6.85 (2 H, d, *J* 10 Hz), 4.85 (1 H, s), and 3.8 (3 H, s); *m/z* 255 (M^+); $\nu_{max.}$(KBr) 3 050m, *ca.* 2 900s, 2 230w cm^{-1} (Found: C, 70.5; H, 5.15; N, 5.5. $C_{15}H_{13}NOS$ requires C, 70.56; H, 5.13; N, 5.49%).

(**28d**): *yellow plates*, m.p. 81—82 °C (from EtOH); $\delta_H(CDCl_3)$ *ca.* 7.0 (8 H, m), 4.25 (1 H, s), 3.8 (3 H, s), and 3.0 (6 H, s); *m/z* 298 (M^+); $\nu_{max.}$(KBr) 3 050m, *ca.* 2 900s, and 2 220w cm^{-1} (Found: C, 68.5; H, 6.1; N, 9.35. $C_{17}H_{18}N_2SO$ requires C, 68.43; H, 6.08; N, 9.39%).

(**28e**): *yellow plates*, m.p. 85—86 °C (from EtOH); $\delta_H(CDCl_3)$ 7.3 (2 H, d, *J* 10 Hz), 6.7 (3 H, m), 6.55 (2 H, d, *J* 10 Hz), 5.95 (2 H, s), 4.65 (1 H, s), 3.0 (6 H, s); *m/z* 312 (M^+); $\nu_{max.}$(KBr) 3 050m, 2 880s, and 2 220w cm^{-1} (Found: C, 65.8; H, 5.1; N, 8.9. $C_{17}H_{16}N_2O_2S$ requires C, 65.36; H, 5.16; N, 8.97%).

(*Z*)-*Cyanostilbenes* (**29**).—*Typical procedure*. To a stirred THF solution (5 ml) of LDA (0.55 mmol) was added compound (**28b**) (0.5 mmol) at −78 °C. After the mixture had been stirred for 0.5 h, benzaldehyde (1 mmol) was added to the mixture. The resulting solution was stirred for an additional 0.5 h, treated with tributylphosphine (1 mmol), and then stirred for 2 h at room temperature. The reaction mixture was worked up by preparative t.l.c. on silica gel using a 4:3 mixture of benzene–hexane as eluant to give the stilbene (**29a**) which was recrystallized from ethanol to give white prisms, m.p. 76—77 °C.[28]

In a similar way, compounds, (**29b**), (**29c**), (**29d**),[29] (**29e**), and (**29f**)[29] were synthesized.

(**29b**): *white prisms*, m.p. 85—86 °C (from EtOH); $\delta_H(CCl_4)$ *ca.* 7.5 (9 H, m) and 2.45 (6 H, s); *m/z* 233 (M^+); $\nu_{max.}$(KBr) 3 020w, 2 900s, and 2 200m cm^{-1} (Found: C, 87.6; H, 6.4; N, 6.0. $C_{17}H_{15}N$ requires C, 87.52; H, 6.48; N, 6.00%).

(**29c**): *white prisms*, m.p. 94—95 °C (from EtOH); $\delta_H(CDCl_3)$ *ca.* 7.5 (9 H, m), 3.9 (3 H, s), and 2.45 (3 H, s); *m/z* 249 (M^+); $\nu_{max.}$(KBr) *ca.* 2 900s and 2 200m cm^{-1} (Found: C, 81.85; H, 6.1; N, 5.6. $C_{17}H_{15}NO$ requires C, 81.90; H, 6.06; N, 5.62%).

(**29e**): *white prisms*, m.p. 96—97 °C (from EtOH); $\delta_H(CCl_4)$ *ca.* 7.5 (9 H, m), 3.85 (3 H, s), and 2.45 (3 H, s); *m/z* 249 (M^+); $\nu_{max.}$(KBr) *ca.* 2 900s and 2 200m cm^{-1} (Found: C, 81.65; H, 6.0; N, 5.6. $C_{17}H_{15}NO$ requires C, 81.90; H, 6.06; N, 5.62%).

References

1 M. Tazaki and M. Takagi, *Chem. Lett.*, 1979, 767; F. Pochat and E. Levas, *Tetrahedron Lett.*, 1976, 1491.
2 A preliminary account of some of this work has been published; M. Kurauchi, T. Imamoto, and M. Yokoyama, *Tetrahedron Lett.*, 1981, **22**, 4985.
3 J. H. Boyer and R. Selvarajan, *J. Am. Chem. Soc.*, 1969, **91**, 6122.
4 T. Minami, F. Takimoto, and T. Agawa, *J. Org. Chem.*, 1976, **41**, 3811; H. Oedinger, F. Moller, and K. Eiter, *Synthesis*, 1972, 591; F. Pochat, *Tetrahedron Lett.*, 1978, 1055; T. Mukaiyama, I. Kuwajima, and K. Ohno, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 1954.
5 S. Watanabe and K. Ichimura, *Chem. Lett.*, 1972, 35; P. R. Gosselin and C. Thal, *Tetrahedron*, 1979, **36**, 1209.
6 F. Toda and M. Kanno, *Bull Chem. Soc. Jpn.*, 1976, **49**, 2643.
7 A preliminary account of some of this work has been published; M. Yokoyama, K. Hoshi, and T. Imamoto, *Chem. Lett.*, 1982, 1615.
8 References are cited in Ref. 7.
9 P. A. Grieco and Y. Yokoyama, *J. Am. Chem. Soc.*, 1977, **99**, 5210.
10 Beilstein, vol. 6, p. 460.
11 Beilstein, vol. 9, p. 422; R. G. R. Bacon and R. G. Guy, *J. Chem. Soc.*, 1961, 2428.
12 Beilstein, vol. 9, II Ergänzungs Werk, p. 286.
13 R. Mayer, S. Scheithauer, and D. Kunz, *Chem. Ber.*, 1966, **99**, 1393.
14 H. Grass and G. Matthey, *Chem. Ber.*, 1964, **97**, 2606.
15 A. M. Khaletshii and A. M. Yanovitskaya, *Zh. Obshch. Khim.*, 1949 **19**, 1193.
16 Beilstein, vol. 9, p. 441.
17 Beilstein, vol. 9, II Ergänzungs Werk, p. 349.
18 Beilstein, vol. 10, p. 191.
19 Beilstein, vol. 9, p. 667.
20 Beilstein, vol. 7, p. 431.
21 Beilstein, vol. 10, p. 755.
22 Beilstein, vol. 7, p. 454.
23 Beilstein, vol. 8, p. 321.
24 Beilstein, vol. 7, p. 830.
25 G. M. Dyson, H. J. George, and R. F. Hunter, *J. Chem. Soc.*, 1927, 442.
26 F. Challenger and A. D. Collins, *J. Chem. Soc.*, 1924, **125**, 1380.
27 Beilstein, vol. 6, p. 340.
28 R. N. McDonald and D. G. Hill, *J. Org. Chem.*, 1970, **35**, 2942.
29 S.S Kulp and C. B. Caldwell, *J. Org. Chem.*, 1980, **45**, 171.

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