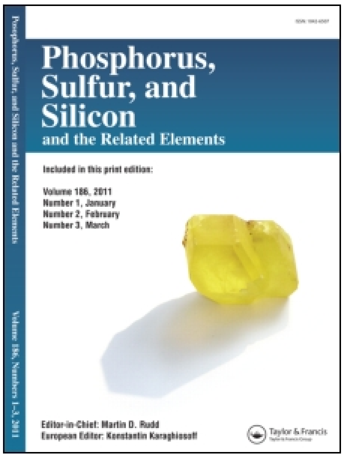

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SYNTHESIS AND REACTIONS OF TRIPHENYLARSINIMINES

Paul Frøyen[a]
[a] Department of Chemistry, Agricultural University of Norway, Ås-NLH, Norway

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SYNTHESIS AND REACTIONS OF TRIPHENYLARSINIMINES

PAUL FRØYEN
Department of Chemistry, Agricultural University of Norway,
P.O. Box 40, 1432 Ås-NLH Norway

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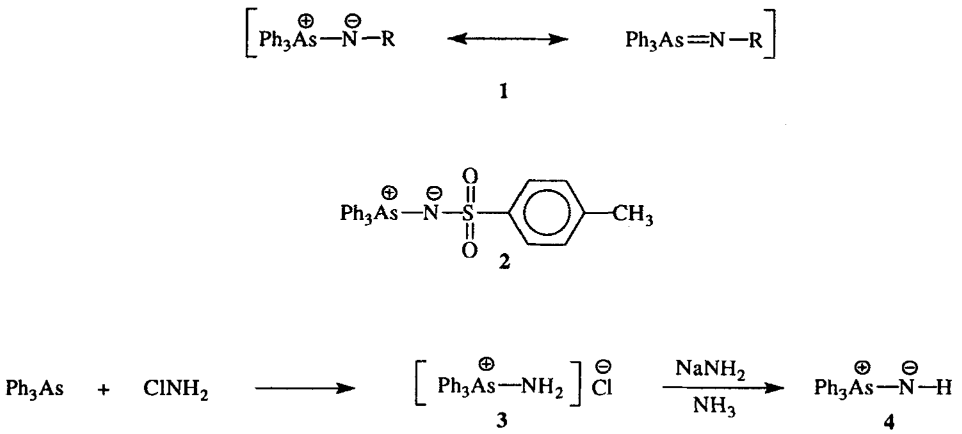
Triphenylarsinimines formed in situ from isocyanates and triphenylarsine oxide have been found to react smoothly with carbonyl compounds like aldehydes, quinones and aromatic ketones giving the corresponding Schiff's bases in high yields. In the case of aldehydes, quinones or activated ketones, e.g., α-diketones, only a catalytic amount of triphenylarsine oxide is necessary for the reaction to proceed to completion. Quinones react with particular ease. Thus the previously unknown 9,10-phenanthrenequinone *N*-phenylimine **12** (R = Ph, Scheme IV) can be prepared in high yield from 9,10-phenanthrenequinone and phenyl isocyanate under catalytic influence of triphenylarsine oxide. Orthoquinones like 9,10-phenanthrenequinone react with vinylic isocyanates, forming monoimines **13** which rearrange to 1,4-oxazines **14** (Scheme V). Diisocyanates react under the catalytic action of triphenylarsine oxide with dialdehydes under mild conditions, forming some interesting new polymers **25**, **26** in high yields. Reactions with aliphatic isocyanates give *N*-alkyl-*N*′-arylcarbodiimides, whereas reactions with isothiocyanates proceed through intermediates **20** and **21** to mixed carbodiimides **16**, **24** and **25**.

Key words: Triphenylarsinimines; synthesis; reactions; Schiff's bases; unsymmetrical carbodiimides; polymers.

In preceding papers[1–3] a new route to a wide range of triphenylarsinimines, including the *N*-phenyl and *N*-(1-naphthyl) derivatives were described, and some of their reactions with carbonyl[3] and nitroso compounds[4] reported for the first time.

Triphenylarsinimines are resonance hybrids of the general structure **1** in which R symbolizes organic or inorganic groups of many sorts (Scheme I). Strongly electron-withdrawing groups attached to nitrogen effectively delocalize its negative charge, thus resulting in enhanced stability toward electrophiles and permits handling without special precautions.



$$\left[\mathrm{Ph_3\overset{\oplus}{As}{-}\overset{\ominus}{N}{-}R} \longleftrightarrow \mathrm{Ph_3As{=}N{-}R}\right]$$

$$\mathrm{Ph_3As} + \mathrm{ClNH_2} \longrightarrow \left[\mathrm{Ph_3\overset{\oplus}{As}{-}NH_2}\right]\overset{\ominus}{\mathrm{Cl}} \xrightarrow[\mathrm{NH_3}]{\mathrm{NaNH_2}} \mathrm{Ph_3\overset{\oplus}{As}{-}\overset{\ominus}{N}{-}H}$$

SCHEME I

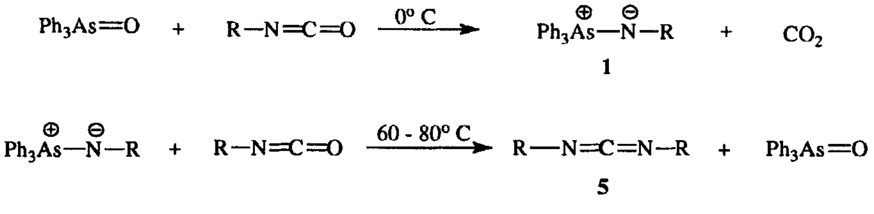
In contrast, when R is hydrogen **4** (Scheme I), the arsenane is very reactive, moisture sensitive, and difficult to store and handle.

The best known members of the class are probably the very stable *N*-tosyliminotriphenylarsenane **2**, the first type of **1** ever reported,[5] and the iminotriphenylarsenane **4** made by Appel *et al.*[6] in a rather laborious synthesis, where the key presursor, aminotriphenylarsonium chloride **3**, requires tedious preparation from chloramine and triphenylarsine, followed by treatment of the intermediate salt with sodamide in liquid ammonia. The latter arsenane, **4**, is less stable than the corresponding phosphorane and especially prone to hydrolysis, thus demonstrating the highly dipolar character and relative weakness of the As—N bond. No reactions with carbonyl compounds were reported, but the imine could be acylated with acyl halides, a reaction typical of ylides and imines, and treatment with hydrogen chloride regenerated the conjugate acid.

Arsinimines stabilized by strongly electron-withdrawing groups, e.g., **2** are unreactive to most electrophiles and do not react with carbonyl compounds. On the other hand, when the group R attached to nitrogen is aryl or vinyl, the arsinimine is moderately stable and undergoes the Staudinger-Meyer-Hauser (aza-Wittig) reaction.[3] The only route to these compounds so far recorded, is via the reaction of As=O compounds with isocyanates.

We showed in three previous papers,[1-3] that triphenylarsine oxide reacts smoothly with isocyanates in solution, forming the corresponding triphenylarsinimines **1** and carbon dioxide in an exotherm reaction (one example of the very rare retro-Wittig reaction), and that the remarkable conversion of isocyanates to carbodiimides **5** with triphenylarsine oxide as catalyst, contrary to expectation can be arrested at this intermediate stage (Scheme II). The further reaction of the intermediate arsinimine with isocyanate needs more forcing conditions. As a rule brief heating of the reaction mixture to about 60–80°C is necessary in order to secure a complete reaction.

The iminoarsenane-forming reaction between triphenylarsine oxide and isocyanates has been carried out in dichloromethane, benzene or toluene at or below room temperature. It should be noticed that iminoarsenanes are most easily formed in the case of isocyanates containing a powerful electron-withdrawing group, with aromatic isocyanates of all kinds and with isocyanates containing a C=C bond in α or β-position to nitrogen. In no case have iminoarsenanes been obtained, however, when R (Scheme II) is an alkyl group. We believe the arsinimine-forming reaction is initiated by a nucleophilic attack of the oxygen of the triphenylarsine oxide at the sp-hybridized carbon of the isocyanate, forming a four membered cyclic intermediate **7** (Scheme III) via the betaine-like structures **6a** and **6b**. It appears that the determining factor for arsinimine formation is the presence of a



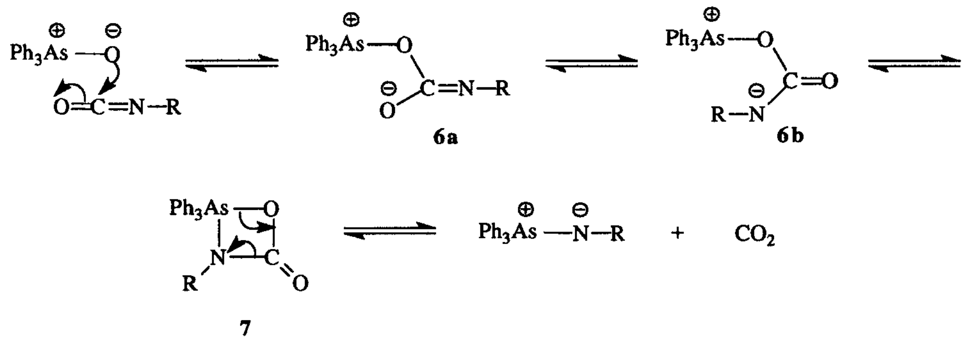
$$Ph_3As{=}O + R{-}N{=}C{=}O \xrightarrow{0^\circ C} Ph_3\overset{\oplus}{As}{-}\overset{\ominus}{N}{-}R + CO_2$$

1

$$Ph_3\overset{\oplus}{As}{-}\overset{\ominus}{N}{-}R + R{-}N{=}C{=}O \xrightarrow{60-80^\circ C} R{-}N{=}C{=}N{-}R + Ph_3As{=}O$$

5

SCHEME II



SCHEME III

R group which is stabilizing the forming negative charge at the N-atom during the concerted breaking of the As—O and C—N bonds of the intermediate as depicted in **7** (Scheme III).

REACTIONS WITH CARBONYL COMPOUNDS

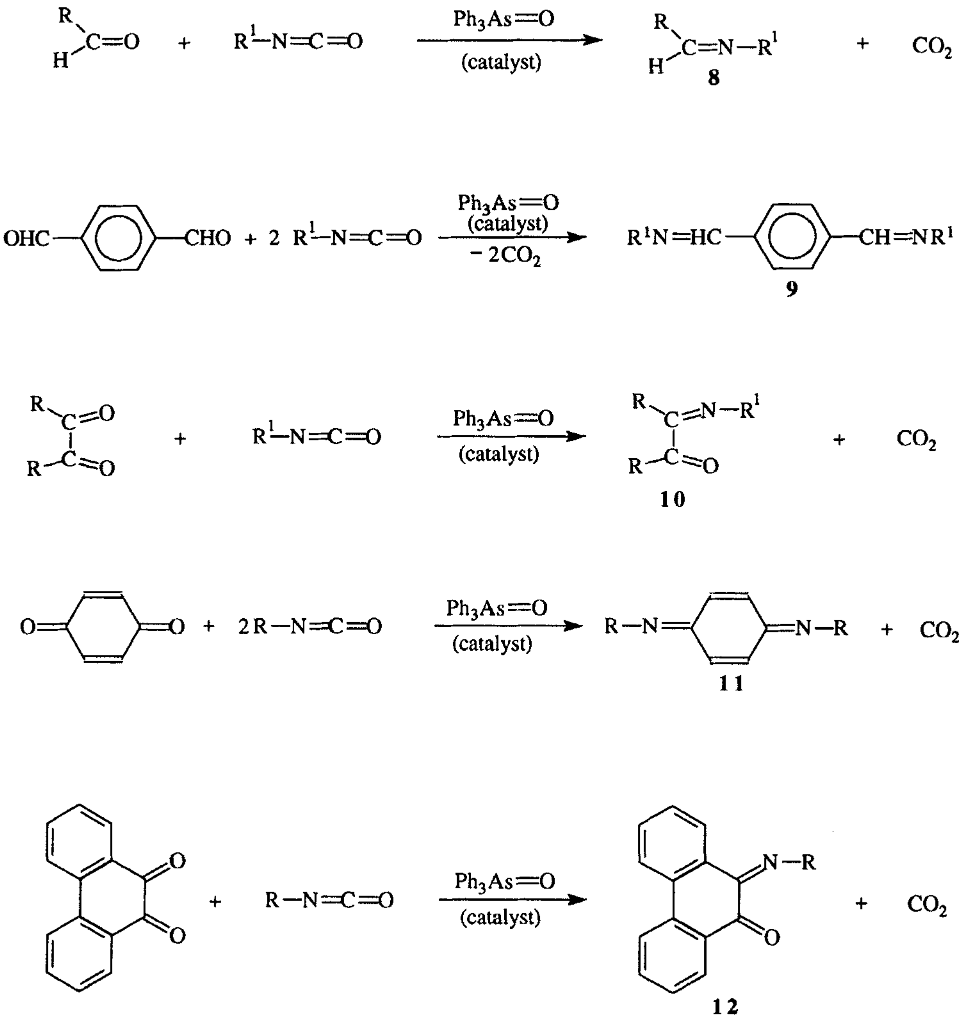
In contrast to the unexpectedly low reactivity towards isocyanates, where arsinimines are several powers of ten less reactive than their phosphorus analogs, they are considerably more reactive than the corresponding phosphinimines towards aldehydes and ketones. This enhanced reactivity of arsinimines towards carbonyl compounds is providing a new route to the $C{=}N{-}R$ entity, in which the isocyanate containing the $={N}{-}R$ moiety is just mixed with an equimolar quantity of the carbonyl compound together with a catalytic amount of triphenylarsine oxide in an inert solvent (Scheme IV). The reactions proceed under mild conditions. Thus the interaction between arsinimines **1** and aldehydes at 20°C affords the corresponding aldimines **8**, **9** in nearly quantitative yields.

The catalytic action of triphenylarsine oxide is also ideally suited for introducing the $={N}{-}R$ moiety into α-dicarbonyl compounds **10**, for quinones and other susceptible multifunctional compounds which are sensitive to the strongly basic and nucleophilic reagents usually applied during established syntheses of their $C{=}N{-}R$ analogs (**11** and **12**, Scheme IV).

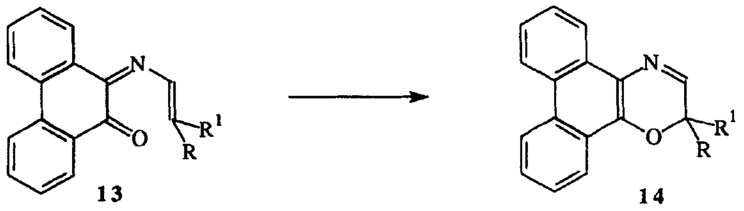
Thus the classical and most common synthesis of ketimines, starting from the corresponding carbonyl compound and a primary amine, fails when applied to quinones.

1,4-Benzoquinone, for instance, does not react with aromatic amines, whereas aliphatic amines give substitution, namely in 2 and 5 position.[8] The reactions of orthoquinones, e.g., 9,10-phenanthrenequinone, with amines are even more complex, leading to a variety of products depending on the structure of reactants and reaction conditions.[9,10] Some of the reactions are supposed to proceed via the corresponding Schiff's bases, but with the exception of a few unsubstituted compounds formed with ammonia, no quinonimine have ever been isolated from these reactions.

In contrast to the above mentioned difficulties, a smooth transformation into quinonimines is observed when quinones are treated according to the present



SCHEME IV



13a $R = R^1 = CH_3$

13b $R = H, R^1 = C_6H_5$

SCHEME V

method with isocyanates in the presence of catalytic amounts of triphenylarsine oxide. Thus 9,10-phenanthrenequinone reacts with vinylic isocyanates under mild conditions, forming monoimines **13** which rearrange to 2*H*-phenanthro (9,10)-1,4-oxazines **14** (Scheme V).

Likewise 1,4-benzoquinone is transformed cleanly and rapidly into the corresponding mono or diimines simply by mixing the starting materials in the right proportions together with a catalytic amount of triphenylarsine oxide.

REACTIONS WITH ISOTHIOCYANATES AND ISOCYANATES: THE FORMATION OF UNSYMMETRICAL CARBODIIMIDES

Carbodiimides are steadily gaining in importance in preparative organic chemistry. Of particular significance is their role as condensing agents in the preparation of peptides and nucleotides. They are most commonly prepared from *N,N'*-disubstituted thioureas by treatment with reagents as diverse as mercuric oxide, lead oxide, sodium amide, SO_2, $SOCl_2$, SO_2Cl_2, SCl_2, S_2Cl_2, phosgene and other rather unpleasant agents. The most convenient route to symmetrical carbodiimides is, however, the very efficient catalytic action of certain phosphine oxides on isocyanates, forming carbodiimides under mild conditions in almost quantitative yields.[7]

The present preparation of arsinimines by means of isocyanates and triphenylarsine oxide, would appear to make it possible to extend this synthetic principle to unsymmetrical carbodiimides also.

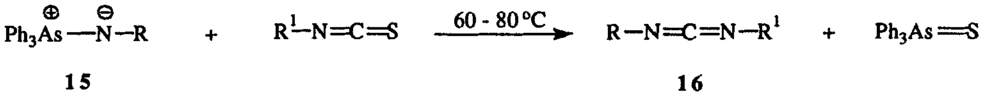
If the reaction between isocyanate and an equivalent amount of triphenylarsine oxide is initially carried out at or below room temperature, no symmetrical carbodiimide is formed. The reaction stops under these conditions at the iminoarsenane stage. The second step of the reaction, leading to an unsymmetrical carbodiimide, could then presumably be performed at elevated temperature by adding an equivalent amount of isothiocyanate (a) or isocyanate (b). The latter (b) gives, in the case of alkyl isocyanates, *N*-alkyl-*N'*-arylcarbodiimides via stable intermediates which require heating to about 200°C to bring about elimination of triphenylarsine oxide. Yields of carbodiimides are rather low, presumably due to polymerization during distillation and under the high temperature elimination of triphenylarsine oxide.

An attempt to isolate the intermediate in a pure state by means of chromatography, gave the corresponding *N,N'*-disubstituted urea together with triphenylarsine oxide (see Experimental). The latter decomposition reflects the extreme ease of hydrolysis under the mildest conditions of these compounds, consistent with the relative weakness of the As—N bond.

In contrast to the slow rate of the final stage in the above mentioned reactions of aliphatic isocyanates, a smooth transformation is observed with their aromatic analogs. The reaction proceeds at 60–80°C affording carbodiimides as shown in Scheme II.

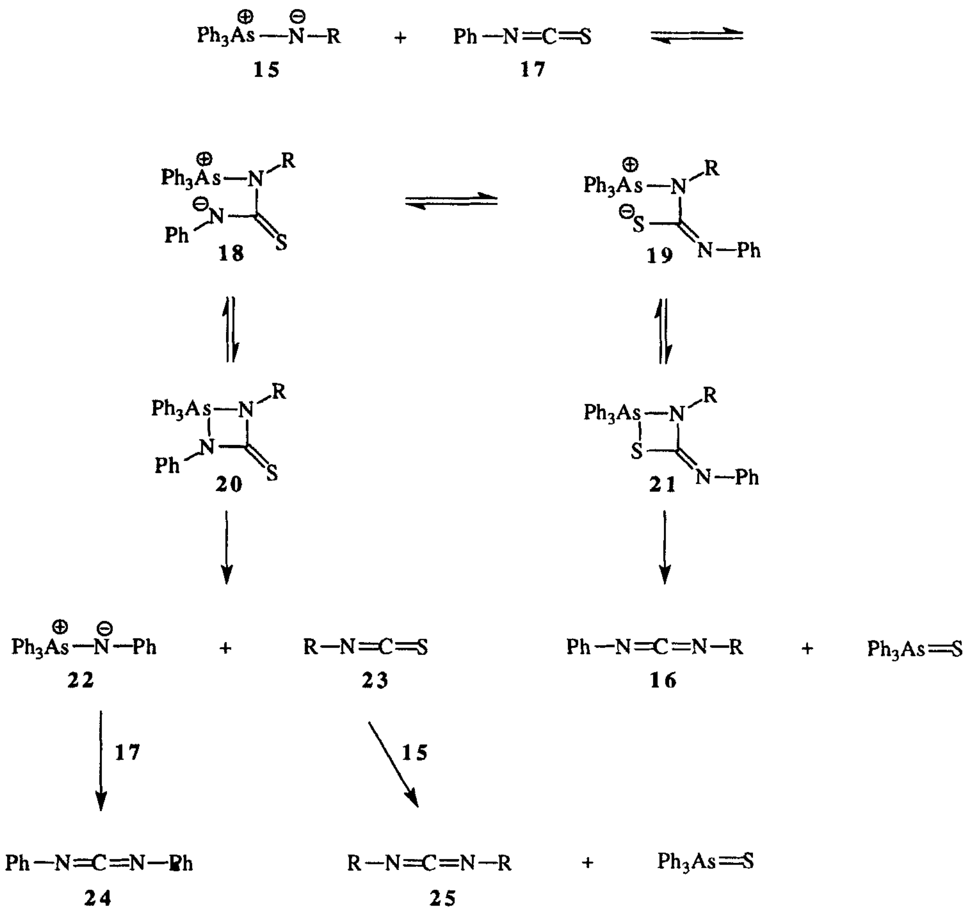
This large difference in reactivity can be ascribed to several factors, partly steric, partly electronic in origin. The sp^2-hybridized carbon atom is increasing the ring strain considerably in the four-membered cyclic transition state. This, in combination with the reduced negative charge on oxygen (due to delocalization through the C=N group), is making the second step critically dependent on the substituents at nitrogen. Presumably, aromatic substituents are providing far better stabilization than alkyl groups for the forming C=N bond, thus mitigating product formation. Similar effects of substituents on the formation of cumulenes have been noted in reactions of phosphonium ylides with ketenes[11] and isocyanates.[12]

Moreover, in the above mentioned case of aromatic isocyanates, the triphenylarsine oxide produced in the second step reacts immediately with the isocyanate, thereby producing a new arsinimine which reacts with a second molecule of isocyanate to give a symmetrical carbodiimide. This is a major drawback of the method, since isolating the desired product implies relatively tedious procedures for the separation of the two carbodiimides produced in the reaction.

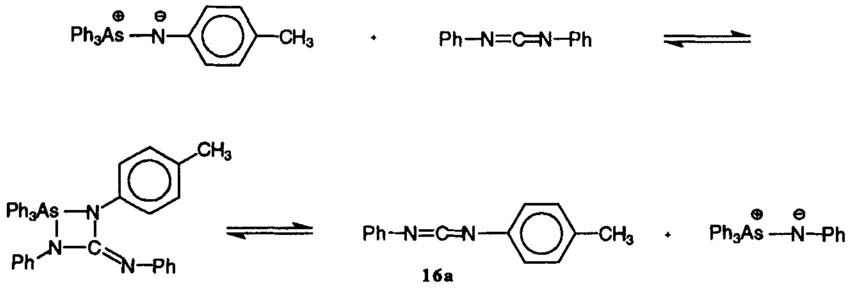


$$\underset{\mathbf{15}}{Ph_3\overset{\oplus}{As}-\overset{\ominus}{N}-R} + R^1-N=C=S \xrightarrow{60-80\,^{\circ}C} \underset{\mathbf{16}}{R-N=C=N-R^1} + Ph_3As=S$$

SCHEME VI



SCHEME VII



SCHEME VIII

In the case of (a), however, a clean cut reaction was expected to ensue, since the triphenylarsine sulfide produced in the second step is a much inferior catalyst compared to triphenylarsine oxide, and thus should be unable to react with isothiocyanates which are poorer electrophiles than the corresponding isocyanates. Accordingly, if an equivalent amount of a suitable isothiocyanate is added to the reaction mixture and the temperature raised to 60–80°C, the second step of the reaction would presumably be completed, leading to the desired unsymmetrical carbodiimide **16** in a clean reaction (Scheme VI).

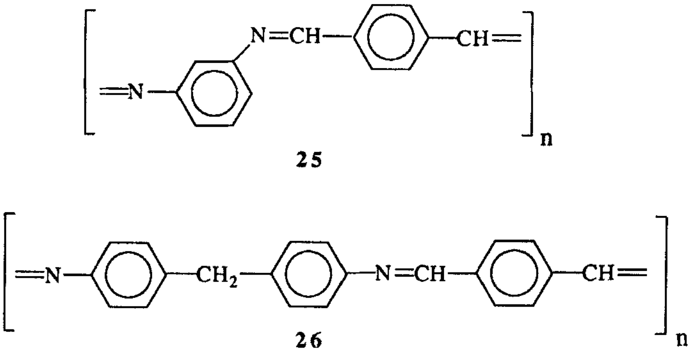
In the event, although unsymmetrical carbodiimides (**16**) are indeed formed as the main product, it soon became clear that the reaction is not clean cut. MS analysis showed the presence of two symmetrical carbodiimides, **24** and **25** besides **16**, suggesting that the reaction proceeds through the alternate transition states **20**, **21** via the corresponding zwitterions **18** and **19** (Scheme VII). Presumably **21** yields the desired unsymmetrical carbodiimide **16**, whereas **20** produces a new arsinimine (**22**) in addition to the isothiocyanate **23**. The former compound (**22**) probably reacts mainly with the starting isothiocyanate **17**, forming the symmetrical carbodiimide **24**. Likewise, the latter compound (**23**) presumably reacts with the starting arsinimine **15**, yielding the symmetrical carbodiimide **25**.

Additionally, since it is reported[13] that diphenylmethylenetriphenylphosphorane reacts with diphenylcarbodiimide forming triphenylketenimine and *N*-phenyliminotriphenylphosphorane, it is necessary to consider the possibility of a reaction between **15** and the forming unsymmetrical carbodiimide (**16**, Scheme VII), leading to a symmetrical carbodiimide through a four membered cyclic intermediate.

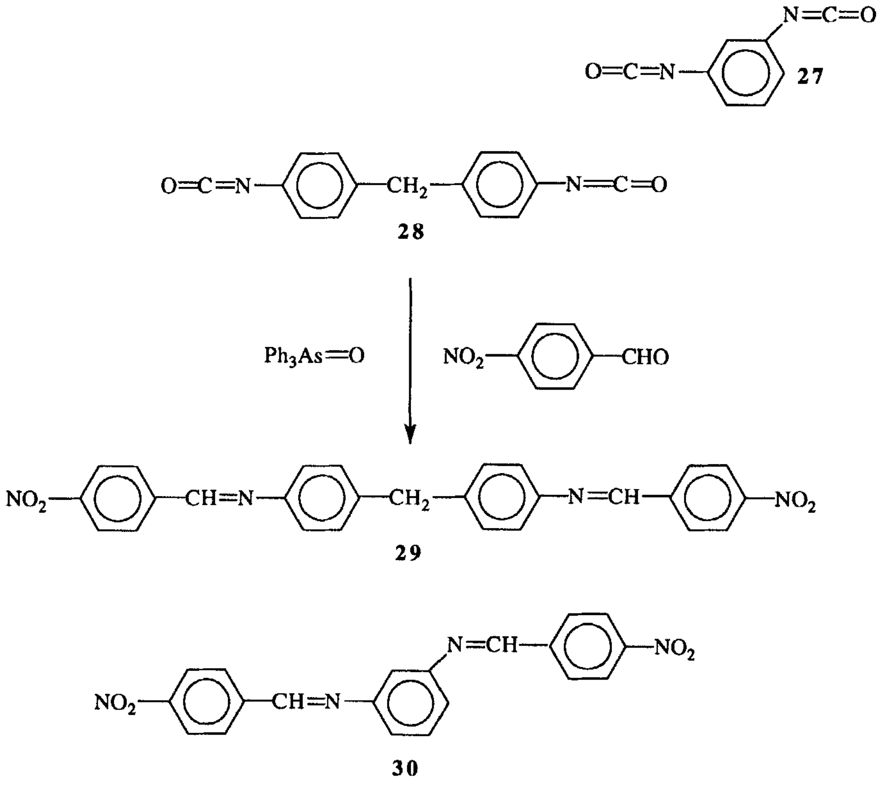
A control experiment where **15** (R = *p*-tolyl) was allowed to react with diphenylcarbodiimide established, however, that the anticipated product, *N*-phenyl-*N'*-*p*-tolylcarbodiimide **16a** (Scheme VIII), was not produced under the experimental conditions employed (brief reflux in benzene). Thus it is suggested that the symmetrical carbodiimides **24** and **25** are formed exclusively via the mechanism vizualized in Scheme VII.

FORMATION OF POLYMERS

The fact that triphenylarsininimines react smoothly with aldehydes at room temperature, whereas the reaction with isocyanates demands more forcing conditions, would appear to open a new route to polymers like **25** and **26** (Scheme IX). In a preliminary study with a view of preparing polymeric Schiff's bases from diisocyanates and dialdehydes, it was found that *p*-nitrobenzaldehyde reacted smoothly with phenylene-1,3-diisocyanate **27** and likewise with methylene bis-(4-phenyl isocyanate) **28** in the presence of triphenylarsine oxide to give Schiff's bases **29** and **30** (Scheme X) in very high yields. It should be pointed out that phosphine oxides are not applicable for the preparation of these compounds as their use lead almost exclusively to polycarbodiimides. Campbell *et al.*[7] report the synthesis of the un-



SCHEME IX



SCHEME X

substituted analogue of the Schiff's base **29** from the catalytic action of an unspecified phospholene oxide on a mixture of **28** and benzaldehyde. The inadequacy of the method is demonstrated by the low yield, only 20%, in spite of the fact that benzaldehyde was used as solvent for the forming nucleophile.

Finally, we allowed diisocyanates **27** and **28** to react with terephthaldehyde in the presence of a catalytic amount of triphenylarsine oxide in refluxing dichloromethane. The subsequent isolation of very high yields of products, sparingly soluble in most organic solvents, confirms the results from the abovementioned control experiments and show the essentially quantitative nature of the reaction. The molecular weight of the formed polymers are as yet undetermined.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectral data were taken at operating frequencies of 60, 200 and 50.3 MHz, respectively, on a Jeol JNM-PXM 60 and a Varian Gemini-200 spectrometer. IR spectra were measured as films with a Perkin Elmer 1310 infrared spectrometer. The mass spectra were obtained on a VG Micromass 7070 F and on a AEI MS-902 mass spectrometer. Column chromatography was carried out over silica gel (Merck No. 9385). The melting points, determined with a Reichert Thermopan melting point microscope, are uncorrected.

Preparation of materials. Triphenylarsine oxide, which was obtained commercially, was freed from water either by azeotropic distillation (benzene, toluene) or by heating at 140–150°C in vacuo until the OH-absorption in the IR spectrum had completely disappeared. The dry product was stored over P_2O_5. Isopropenyl isocyanate and styryl isocyanate were prepared by reaction of methacrylyl chloride and cinnamoyl chloride, respectively, with sodium azide in acetone[14] at 0°C, followed by Curtius rearrangement of the formed azides.

4-Nitrobenzylidene allylimine **8a**, *4-nitrobenzylidene 4-methylaniline* **8b**, and *4-nitrobenzylidene 4-chloroaniline* **8c** were prepared from 4-nitrobenzaldehyde (0.15 g, 1 mmol), and 1.0 mmol) of allyl, *p*-tolyl and *p*-chlorophenyl isocyanate, respectively, together with a catalytic amount of triphenylarsine oxide in dichloromethane (2.0 ml). The reaction mixture was heated under reflux for 5–10 min. Cooling and addition of a little hexane produced immediate crystallization of the aldimine in yields well above 90%. **8a**: m.p. 62°C; MS (70 eV: m/z (%) 190 (21.7, M^+), 189 (32.3), 173 (33.5), 162 (11.2), 149 (12.6), 143 (22.2), 117 (14.6), 116 (27.1), 103 (10.9), 90 (11.7), 89 (25.5), 63 (10.9). **8b**: m.p. 124°C. Lit.[8] 123°C; MS (70 eV): m/z (%) 262 (38.4), 261 (26.4), 260 (100, M^+), 259 (28), 215 (14.2), 213 (42), 152 (15.3), 138 (21.7), 113 (10.8), 111 (33), 76 (20.6), 75 (24.5). **8c**: m.p. 134°C. Lit.[9] 128°C; MS (70 eV): m/z (%) 241 (18.1), 240 (100, M^+), 194 (11.9), 193 (53.9), 165 (10.6), 152 (12), 118 (47.7), 96 (14.7), 92 (24.5), 91 (100), 90 (31.9), 89 (51.1).

Terephthaldehyde bis(4-methyl benzenimine) **9**. To triphenylarsine oxide (0.10 g, 0.3 mmol) in benzene is added *p*-tolyl isocyanate (1.33 g, 10 mmol) and terephthaldehyde (0.67 g, 5.0 mmol). The mixture was heated at about 50°C for 5 minutes with vigorous stirring until CO_2 evolution had ceased. The temperature was finally increased to 81°C for a brief period in order to secure a complete reaction. The reaction mixture was cooled and allowed to stand overnight at room temperature. The next day the product (1.50 g, 96%) was separated and recrystallized from acetone/ethanol **9**: m.p. 195°C; MS (70 eV): m/z (%) 312 (100, M^+), 256 (21), 228 (7.9), 194 (11), 171 (10.5), 167 (10), 156 (15.1), 123 (22.5), 121 (28.3), 115 (12.9), 113 (13.2), 112 (12.3), 111 (19.9), 110 (15.9), 109 (19.8), 107 (11.9), 101 (13.9), 99 (15), 98 (21.6), 97 (35.6).

1,2-Diphenyl-2-phenylimino ethanone. (**10a**, $R = R^1 = Ph$). Benzil (0.21 g, 1 mmol) was added to a stirred solution of triphenylarsine oxide (30 mg, 0.1 mmol) and phenyl isocyanate (0.12 g, 1 mmol) in dry benzene (20 ml) and heated at 50–70°C until evolution of CO_2 was over, whereafter the reaction temperature was briefly raised to 81°C. The solvent was evaporated at reduced pressure, and the product extracted with ether and recrystallized. Yield 225 mg (93%) **10a**: m.p. 104°C. Lit.[15] 103–106°C; MS (70 eV): m/z (%) 285 (3.1, M^+), 180 (22.6, M-PhCO), 179 (100), 77 (66.5).

3-Phenylimino-2-butanone. (**10b**, $R = Ph$, $R^1 = CH_3$) To a stirred solution of triphenylarsine oxide (0.1 g, 0.3 mmol) in dry benzene (10 ml) was added phenyl isocyanate (0.6 g, 5 mmol) and 2,3-

butanedione (0.43 g, 5 mmol). The reaction mixture was heated at 60–70°C for 30 min, the solvent stripped, and the remaining yellow oil distilled in a Kugelrohr apparatus. Yield 0.72 g **10b**: MS (70 eV): m/z (%) 161 (8.2, M^+), 119 (13.1), 118 (100, M-CH_3CO), 93 (10.4), 77 (83.6).

1,2-Diphenyl-((2-phenylethylene-)-1-imino) ethanone **10c** was prepared as described above from benzil (0.21 g) and styryl isocyanate (0.14 g) at 40°C. Yield 120 mg of **10c**: m.p. 110°C. MS analysis gave a molecular ion (32%) at m/z 311, and the main peak at m/z 206 (M-PhCO, 100%).

N,N'-Cyclohexa-2,5-diene-1,4 diylidene-bis-benzenamine **11**. 1,4-Benzoquinone (5 mmol, 0.54 g) was added to a stirred solution of triphenylarsine oxide (0.2 mmol, 0.17 g) and phenyl isocyanate (10 mmol, 1.19 g) in 10 ml of dry benzene. The reaction mixture was heated for 30 min at 60–65°C until CO_2 evolution had ceased, whereafter the solvent was evaporated and the residue extracted with ether. The ether extract was concentrated and the product crystallized from ether/pentane. Recrystallization from ethanol afforded 1.25 g (97%) of **11**; m.p. 179°C, undepressed by admixture of an authentic sample. Lit.[16] m.p. 176–80°C.

10-Benzenimino-10H-phenanthrene-9-one **12** was prepared as described in the above procedure from 9,10-phenanthrenequinone, phenyl isocyanate and triphenylarsine oxide: m.p. 93°C; MS (70 eV): m/z (%) 284 (17.8), 282 (71, M^+), 255 (70, M-CO), 254 (100), 194 (15), 180 (35.5), 164 (11.4), 163 (15.5), 152 (10), 151 (12.2), 140 (21.4), 103 (11), 77 (16.4).

2,2-Dimethyl-phenanthro (9,10)-1,4-oxazine **14a** was prepared as described above from 9,10-phenanthrenequinone (0.52 g, 2.5 mmol) and isopropenyl isocyanate (0.25 g, 2.5 mmol) together with a catalytic amount of triphenylarsine oxide. The solvent was evaporated to give a yellow oil which was chromatographed on silica gel. Elution with a mixture of toluene and petroleum ether gave 0.25 g (38%) of a crystalline product: m.p. 114–115°C; ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.50 (s, 6H, CH_3), δ 7.43–7.75 (m, 5H, $H_{aromatic}$), δ 8.20–8.82 (m, 3H, $H_{aromatic}$); MS (70 eV): m/z (%) 260 (21.6, $M^+ + 1$), 259 (100, M^+), 164 (30), 165 (25.2); IR (film) ν 3070 (m, $H_{aromatic}$), 2970 (m, $H_{aliphatic}$), 1620 (w), 1570 (s, C=C), 1495 (w), 1450 (m), 1430 (m), 1350 (m), 1320 (s), 1245 (m), 1210 (s), 1153 (s), 1110 (s), 1012 (s), 753 (s), 722 (s).

2H-phenanthro (9,10)-2-phenyl-1,4-oxazine **14b** were similarly prepared from 9,10-phenanthrenequinone (0.52 g, 2,5 mmol), cinnamene isocyanate (0.36 g, 2.5 mmol) and a catalytic amount of triphenylarsine oxide in benzene. The solvent was evaporated in vacuo and the residue chromatographed on silica gel. Elution with a mixture of chloroform and hexane (1:1) gave after recrystallization from dichloromethane/ether 0.31 g (40%) of **14b**; m.p. 127°C; MS (70 eV): m/z (%) 310 (23.4, $M^+ + 1$), 309 (100, M^+), 308 (23.6), 280 (32.7, M-HCO), 219 (38.5, M-PhCH), 190 (12.2), 165 (12.9), 164 (16.3), 163 (21.9), 105 (24), 91 (23), 77 (15.2). No carbonyl band was detected by infrared.

*Attempted synthesis of N-phenyl-N'-p-*tolylcarbodiimide **16a**. To a suspension of 5.0 mmol triphenylarsine oxide in 10 ml benzene is added dropwise with vigorous stirring 5.0 mmol *p*-tolyl isocyanate. The arsinimine-forming reaction is completed in a few minutes at ambient temperature, whereafter 5.0 mmol phenyl isothiocyanate is added and the temperature raised to 81°C (reflux) for a couple of minutes. The reaction mixture is cooled a little and pentane (30 ml) is added. Precipitated triphenylarsine sulfide (1.60 g) is then separated by filtration after being allowed a brief time for crystallization. Evaporation of the solvent followed by distillation (Kugelrohr) gave carbodiimide (1.0 g 96%) which polymerized after a couple of days at room temperature. IR (film) 2120 cm^{-1} (N=C=N). MS (70 eV): m/z (%) 222 (58.5, M^+, bis-(4-methylphenyl)-carbodiimide)), 208 (100, M^+, N-4-methylphenyl-N'-phenylcarbodiimide, **16a**), 194 (43.3, M^+, diphenylcarbodiimide).

Attempted synthesis of N-benzyl-N'-phenylcarbodiimide **16b**. Triphenylarsine oxide (1.62 g, 5.0 mmol), phenyl isocyanate (0.60 g, 5.0 mmol) and benzyl isothiocyanate (0.75 g, 5.0 mmol) was dissolved in benzene and heated as described in the above procedure for **16a**. Distillation gave 0.42 g (40%) of mixed carbodiimides; ^{1}NMR (200 MHz, $CDCl_3$) δ 4.72 (s, 2H, CH_2), δ 7.2–7.5 (m, 10H, $H_{aromatic}$); IR (film) 2120 cm^{-1} (N=C=N); MS (70 eV): m/z (%) 208 (31.9, M^+, **16b**), 194 (70.8, M^+, diphenylcarbodiimide). The main part of the product polymerized during distillation.

Attempted synthesis of N-allyl-N'-p-tolylcarbodiimide **16c**. *P*-Tolyl isocyanate (0.62 g, 5.0 mmol), triphenylarsine oxide (5.0 mmol) and allyl isothiocyanate (0.50 g, 5.0 mmol) was dissolved in dry benzene and treated as described above. Distillation (Kugelrohr, 0.01 mm Hg) gave 0.35 g of product (the main part polymerized during distillation). ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.32 (s, 3H, CH_3), δ 4.01 (d, *J* 5.5 Hz, 2H, CH_2), δ 5.20–5.42 (q, 2H, CH_2), δ 5.86–6.08 (m, 1H, CH), δ 7.02–7.34 (m, 4H, $H_{aromatic}$, IR (film) 2120 cm^{-1} (N=C=N); MS (70 eV): m/z (%) 222 (9.8, M^+, bis-(4-methylphenyl)-carbodiimide), 172 (78.4, M^+, **16c**).

Attempted synthesis of N-4-bromophenyl-N'-4-methylphenylcarbodiimide **16d**. Triphenylarsine oxide (0.65 g, 2.0 mmol) was suspended in benzene (10 ml). *P*-Tolyl isocyanate (0.26 g, 2 mmol) was added under vigorous stirring and the reaction mixture held at room temperature until gas evolution had ceased. The reaction mixture was thereafter heated to 60–80°C, a solution of 4-bromophenyl isothiocyanate (0.42 g, 2.0 mmol) was added and the temperature held at 81°C for 5 minutes. A sample withdrawn for IR analysis absorbed strongly at 2120 cm^{-1} (N=C=N). The mixture was cooled a little and a solution of oxalic acid (0.18 g, 2.0 mmol) in 3 ml dioxane added in one portion with continuous stirring. The mixture was briefly heated, and thereafter cooled. The crystalline product, presumably *N*-4-bromophenyl-*N'*-4-methylphenylurea was removed by filtration and recrystallized from acetone/ethanol. MS analysis showed the product to be a mixture of three compounds with following molecular ions; m/z (%) 370 (8.1, M^+, bis-(4-bromophenyl)urea), 304 (38.5, M^+, *N*-4-bromophenyl-*N'*-4-methylphenylurea), 240 (76.1, M^+, bis-(4-methylphenyl) urea).

16e: To a solution of triphenylarsine oxide (1.70 g, 5 mmol) in benzene (10 ml) was added *p*-tolyl isocyanate (0.66 g, 5 mmol) under vigorous stirring. When the evolution of CO_2 had ceased, *n*-propyl isocyanate (0.43 g, 5 mmol) was added, and the temperature gradually increased to 80°C. After 30 min gentle reflux, the solvent was evaporated at reduced pressure, and the resulting stable intermediate heated at 200–220°C (0.001 mmHg) in a Kugelrohr apparatus. The decomposition/distillation yielded 0.21 g (24%) **16e**: IR (film) 2060 cm^{-1} (strong);

In a later experiment an attempt was made to characterize the aforementioned intermediate. The isolated product, a yellow oil was set aside for 3 days, whereafter it crystallized. The solid compound was chromatographed on silica gel. Elution with a mixture of ether and ethyl acetate (10:1) gave, besides triphenylarsine oxide, a product which melted at 125°C and was shown by its spectroscopic properties to be *N*-4-methylphenyl-*N'*-propylurea: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, 3H, CH_3), δ 1.46 (q, 2H, CH_2), δ 2.28 (s, 3H, CH_3), δ 3.13 (t, 2H, CH_2), δ 7.03–7.17 (m, 4H, $H_{aromatic}$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 12.25, 21.65, 24.25, 42.72 ($C_{aliphatic}$), δ 121.45, 129.95, 133.25, 136.60 ($C_{aromatic}$), δ 157.26 (C=O).

N,N'-bis(4-nitrobenzylidene)-4,4-diaminodiphenylmethane **29**. To methylene bis-(4-phenyl isocyanate) (1 mmol, 0.25 g) in dichloromethane (5 ml) was added 4-nitrobenzaldehyde (2 mmol, 0.30 g) and a catalytic amount of triphenylarsine oxide. The reaction mixture was vigorously stirred and held at 40°C for 15 min. The mixture was thereafter cooled to room temperature and the precipitated product separated to give, together with a later crop of crystals, 0.43 g (93%) of **29**; m.p. 227°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 4.05 (s, 2H, CH_3), δ 7.36 (m, 8H, $H_{aromatic}$), δ 8.18–8.41 (m, 8H, $H_{aromatic}$), δ 8.84 (s, 2H, HC=N); MS (70 eV): m/z (%) 465 (16.6, M^+ + 1), 464 (55.6, M^+), 434 (11.1), 325 (31.2), 193 (12.8), 165 (18.2), 77 (13.1), 69 (13.7), 62 (20.1).

N,N'-bis-(4-nitrobenzylidene)-1,3-diaminobenzene **30**. Similarly prepared in nearly quantitative yield from 1,3-phenylene diisocyanate (2 mmol, 0.32 g) and 4-nitro benzaldehyde (4 mmol, 0.61 g) with triphenylarsine oxide as catalyst, were **30**, a yellow crystalline product which defied attempts at recrystallization. ^{1}H NMR (200 MHz, DMSO-d_6) δ 7.30 (m, 4H, $H_{aromatic}$), δ 8.10–8.50 (m, 8H, $H_{aromatic}$), δ 8.94 (s, 2H, HC=N); MS (70 eV): m/z (%) 375 (14.8, M + 1), 374 (63.7, M^+), 313 (14.5), 241 (11.7), 179 (12.9), 178 (10).

Reaction of terephthaldehyde with methylene bis-(4-phenyl isocyanate). To a solution of terephthaldehyde (0.27 g, 2 mmol) in dichloromethane was added methylene bis-(4-phenyl isocyanate) (0.54 g, 2 mmol) and a catalytic amount of triphenylarsine oxide. The reaction mixture was refluxed with stirring for 30 min. An infrared spectrum of the solution confirmed the expected structure and showed the complete absence of isocyanate, carbodiimide and carbonyl bands. The solvent was evaporated giving a yellow crystalline product which defied recrystallization and after trituration and repeated washings with acetone yielded 0.56 g (95%) of **26**: m.p.: melting started, but incomplete at 350°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.08 (s, 2H, CH_2), δ 7.10–7.40 (m, 8H, $H_{aromatic}$), δ 7.95–8.15 (m, 4H, $H_{aromatic}$), δ 8.14 (d, 1H, CH); IR (film) 1690 cm^{-1} (strong).

Reaction of terephthaldehyde with 1,3-phenylene diisocyanate. To a stirred solution of 1,3-phenylene diisocyanate (0.32 g, 2 mmol) and terephthaldehyde (0.27 g, 2 mmol) in dichloromethane (20 ml) was added a catalytic amount of triphenylarsine oxide. The mixture was refluxed for 30 min, whereafter the solvent was evaporated. The resulting polymer **25** (0.40 g, 98%) was triturated and washed with acetone. The yellow crystalline product, which was very difficult to recrystallize, absorbed strongly at 1690 cm^{-1}. The IR spectrum showed no bands in the region 2100–2250 cm^{-1} (isocyanate, carbodiimide).

M.p.: over 350°C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.27 (s, 1H, $H_{aromatic}$), δ 7.30–7.75 (m, 3H, $H_{aromatic}$), δ 8.03–8.09 (m, 4H, $H_{aromatic}$), δ 8.61 (d, 2H, CH=N).

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