Mahoney and DaRooge [10] have conducted thermodynamic studies on the equilibria between different phenols and phenoxy radicals and found that electron-withdrawing substituents raise the OH-bond energy. In the present case, this means that acetoguaiacone will be favoured at equilibrium and that the main reaction products will be those of radical *1b*.

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A Synthesis of Azobenzenes from Triphenylarsine Phenylimine and Nitrosobenzenes

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The similarity between the nitroso group and the carbonyl group in the reaction with phosphonium ylides and phosphonate carbanions has been demonstrated by several workers.[1-3] Attempts to react phosphine imines with nitrosobenzene have failed, however.[4] The present author has found that triphenylarsine phenylimine reacts with nitrosobenzenes under mild conditions to give excellent yield of azobenzenes.

$$Ph_3\overset{+}{A}s-\overset{-}{N}Ph + ArNO \rightleftharpoons Ph_3As(-O-)(-NPh-)NAr \rightarrow Ph_3As=O + PhN=NAr$$

(*1*)

The mechanism of the reaction between triphenylarsine phenylimine and the nitroso compounds is expected to parallel rather closely that of the Wittig reaction between stabilized ylides and carbonyl compounds. Presumably, the reaction is initiated by a nucleophilic attack of the arsine imine on the nitrogen atom of the nitroso compound, synchronized with an attack by the oxygen of the nitroso group on arsenic. The penta-covalent cyclic intermediate (*1*) thus formed undergoes decomposition to arsenic oxide and azobenzene. The reactivity of the nitroso compounds in the reaction with triphenylarsine phenylimine decreases in the order *p*-nitronitrosobenzene > *p*-chloronitrosobenzene > nitrosobenzene > *p*-dimethylaminonitrosobenzene. The same order of reactivity was found in the Wittig reaction between the stabilized ylides fluorenylidene resp. phenacylidene triphenylphosphorane and *para*-substituted benzaldehydes.[5,6]

In connection with the preparation of *p*-nitroazobenzene an attempt was made to solve the disagreement between the physical data reported for *o*-nitroazobenzene.[7,8]

o-Nitroazobenzene isolated from the present reaction between *o*-nitronitrosobenzene and triphenylarsine phenylimine had after two recrystallisations from ethanol m.p. 70–71° and is doubtless identical with the compound made by Bamberger and Hübner.[7] Thin-layer chromatography showed, besides triphenylarsine oxide, a single reaction product. No sign of isomerisation could be detected when the *o*-nitroazobenzene was irradiated with ultraviolet light and afterwards analysed by thin-layer chromatography. In a previous study of the reaction between triphenylarsine phenylimine and carbonyl compounds [9] it was assumed that triphenylarsine phenylimine was more nucleophilic than its phosphorus analogue. This assumption is confirmed by the

present findings. The higher reactivity of triphenylarsine phenylimine may indicate, less contribution from the ylene structure: $Ph_3X=NPh$, in the resonance hybrid: $Ph_3X=NPh \leftrightarrow Ph_3\overset{+}{X}-\overset{-}{N}Ph$, of triphenylarsine phenylimine than in its phosphorus analogue. Studies of fluorenylidene triphenylarsenane and the analogous phosphorane [10,11] have led to a similar conclusion as to the reason for the higher reactivity of the arsenic ylide.

Experimental. Nitrosobenzene (m.p. 68°),[12] *p*-nitronitrosobenzene (m.p. 119°),[13] *p*-dimethylaminonitrosobenzene (m.p. 87.8°),[14] *p*-chloronitrosobenzene (m.p. 88°),[15] and *o*-nitronitrosobenzene (m.p. 126°),[16] were prepared as described in the literature.

p-*Nitroazobenzene.* To a solution of 0.5×10^{-2} mol of triphenylarsine phenylimine made from 50 ml absolute benzene, 1.60 g triphenylarsine oxide, and 0.60 g phenyl isocyanate,[9] was added 0.76 g, 0.5×10^{-2} mol, of *p*-nitronitrosobenzene. The reaction mixture was heated for a few minutes, whereafter most of the benzene was distilled off. The product was treated with ether and most of the triphenylarsine oxide was filtered off. The yield of *p*-nitroazobenzene was about 80 %. After two recrystallizations from ligroin the melting point was 134°, lit.[17] 134–135°.

p-*Chloroazobenzene.* 0.5×10^{-2} mol of the triphenylarsine phenylimine prepared as previously described [9] was dissolved in 30 ml absolute benzene and 0.5×10^{-2} mol of *p*-chloronitrosobenzene was added. The reaction mixture was heated for 2 h. Otherwise, the same procedure was followed as described for *p*-nitroazobenzene. The product was recrystallized from ethanol, yield 0.75 g, m.p. 90°, lit.[18] 90–91°.

Azobenzene. The same procedure was followed as described above. The reaction mixture was heated during several hours before the colour changed from green-yellow to red. The reaction could also be performed at room temperature when the reaction mixture was allowed to stay for a month under dry nitrogen. The product was analyzed by thin layer chromatography and was shown to be a mixture of *cis* and *trans* azobenzene by comparison with authentic samples.

p-*Dimethylaminoazobenzene.* The synthesis was performed as described above. The reaction mixture was heated during 72 h, but the green colour of the nitroso compound was still dominant, and the reaction far from completed. Chromatographic analysis showed the presence of *p*-dimethylaminoazobenzene together with unreacted *p*-dimethylaminonitrosobenzene and triphenylarsine phenylimine.

o-*Nitroazobenzene.* *o*-Nitronitrosobenzene (0.36 g) in dry benzene was added to a solution of 0.68 g triphenylarsine phenylimine in benzene. The mixture was heated for 5–10 min, whereafter the benzene was distilled off. The product (0.4 g) had m.p. 70–71° after two recrystallizations from ethanol. On admixture of the compound made by the method of Bamberger and Hübner [7] the melting point was undepressed.

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