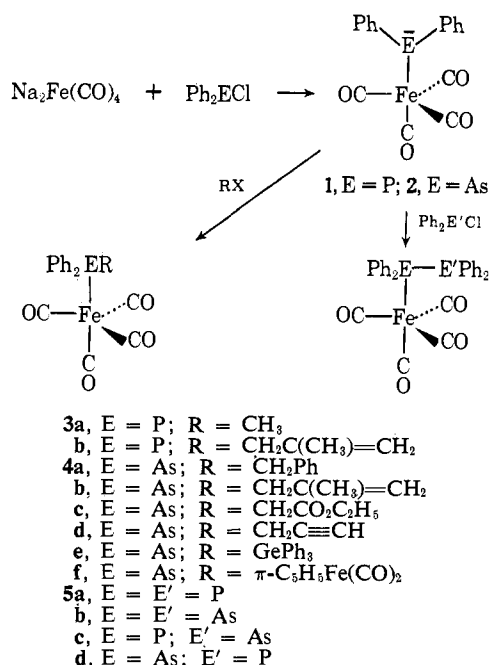


phosphide and arsenide complexes **1** and **2** and their facile *in situ* transformation into neutral phosphine and arsine complexes (Scheme I). These simple syn-

Scheme I



thetic schemes have yielded some unusual derivatives.

Reaction of  $\text{Na}_2\text{Fe}(\text{CO})_4$  with  $\text{Ph}_2\text{PCl}$  or  $\text{Ph}_2\text{AsCl}$  (1 equiv each in THF) affords **1** or **2** which have been isolated and fully characterized (elemental analyses and ir and pmr spectra) as yellow crystalline  $[(\text{Ph}_3\text{P})_2\text{N}]^+$  salts. The  $\nu_{\text{CO}}$  patterns for **1** and **2** (2004, 1910, and 1893  $\text{cm}^{-1}$  in acetone for **1** and 1999, 1910, and 1890 for **2**) are consistent with the expected trigonal-bipyramidal coordination in which the  $\text{Ph}_2\text{E}$  group occupies an axial position. X-Ray crystallographic studies are planned.

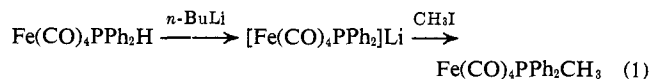
Complexes **1** and **2** are potentially ambient nucleophiles (at Fe or P-As) but *in situ* alkylation occurs exclusively at P or As affording monomeric phosphine or arsine complexes **3** and **4** (Scheme I) in respectable (53–72%) yields.<sup>5</sup>

In a typical preparation of **3** or **4**, 1 mmol of chlorodiphenylarsine was added dropwise to a stirred suspension of  $\text{Na}_2\text{Fe}(\text{CO})_4$  in 15 ml of THF at 25° under nitrogen. After 15 min, 1.2 mmol of 3-chloro-2-methylpropene was added to the yellow solution and stirring was continued for an additional 15 min. The THF was removed *in vacuo* and the residue was recrystallized from methanol or methanol-water giving 301 mg (67%) of the diphenylmethallylarsine complex, **4b**, mp 121–123°; ir ( $\text{CHCl}_3$ ): 2053, 1971, 1940 (terminal CO on iron), and (KBr) 1640  $\text{cm}^{-1}$  ( $\nu_{\text{C}=\text{C}}$ ); nmr ( $\text{CDCl}_3$ ):  $\delta$  1.52 (s, 3 H), 3.28 (s, 2 H), 4.95 (d, 2 H,  $J = 4.5$  cps), 7.5 (m, 10 H). This method is a simpler version of the two-step sequence recently reported by Treichel requiring the prior isolation of the diphenylphosphine complex (eq 1).<sup>6,7</sup> The versatility of our method is il-

(5) No attempt has been made to maximize yields from these single flask, 1 mmol scale reactions.

(6) P. M. Treichel, W. K. Dean, and W. M. Douglas, *Inorg. Chem.*, **11**, 1609 (1972).

(7) P. M. Treichel, W. M. Douglas, and W. K. Dean, *ibid.*, **11**, 1615 (1972).



lustrated by the wide range of phosphine and arsine complexes prepared in this way (Scheme I). Of special interest is the use of this method to introduce into **3** and **4** R groups having functionality capable of serving as a ligand, e.g.,  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2$ , **3b** and **4b** and  $\text{HC}\equiv\text{CCH}_2$ , **4d**. The spectral properties of these complexes indicate no interaction between the saturated metal and these neighboring latent ligands. The preparation of novel heterometallic bridging arsenide complexes **4e** ( $\nu_{\text{CO}} = 2045, 1965$ , and  $1940 \text{ cm}^{-1}$ ) and **4f**<sup>8</sup> ( $\nu_{\text{CO}} = 2040, 2025, 1988, 1948$ , and  $1927 \text{ cm}^{-1}$ ) further illustrates the versatility of this method.

Reaction of **1** or **2** with an additional equivalent of  $\text{Ph}_2\text{PCl}$  or  $\text{Ph}_2\text{AsCl}$  affords a general synthesis of diphosphine, diarsine, or mixed phosphine-arsine complexes **5a–d** which have been isolated and fully characterized (Scheme I). A few diarsine and diphosphine complexes have been previously isolated<sup>9–11</sup> and characterized, but mixed phosphine-arsine complexes have not been described. The  $\nu_{\text{CO}}$  patterns for **5a–d** closely resemble those of the simple phosphine and arsine derivatives **3** and **4** suggesting a similar coordination geometry and no direct interaction between the saturated iron and the terminal P or As. The presence of two <sup>31</sup>P doublets ( $\delta$  61.5 and 2.98,<sup>12</sup>  $J_{\text{P-P}} = 322.5$  Hz) in the diphosphine complex **5a** is consistent with this idea and shows that the iron does not migrate from one phosphorus to the other on the nmr time scale. The mixed phosphine-arsine complexes exhibit distinctive <sup>31</sup>P spectra (singlets at  $\delta$  57.8 and 10.7 for **5c** and **5d**, respectively) demonstrating their separate identities and confirming our expectation that the individual isomers do not interconvert under ambient conditions over prolonged periods.

**Acknowledgments.** We thank the National Science Foundation (Grant No. GP20273X) for financial support of this work and John Shapley for suggestions.

(8) R. J. Haines, C. R. Nolte, R. Greatrex, and N. N. Greenwood, *J. Organometal. Chem.*, **26**, C45 (1971).

(9) W. Hieber and R. Kummer, *Chem. Ber.*, **100**, 148 (1967).

(10) W. Hieber and W. Opavsky, *ibid.*, **101**, 2966 (1968).

(11) F. G. A. Stone, M. Green, and A. Taunton-Rigby, *J. Chem. Soc. A*, 1875 (1969).

(12)  $\text{H}_3\text{PO}_4$  is the reference and the protons have been decoupled.

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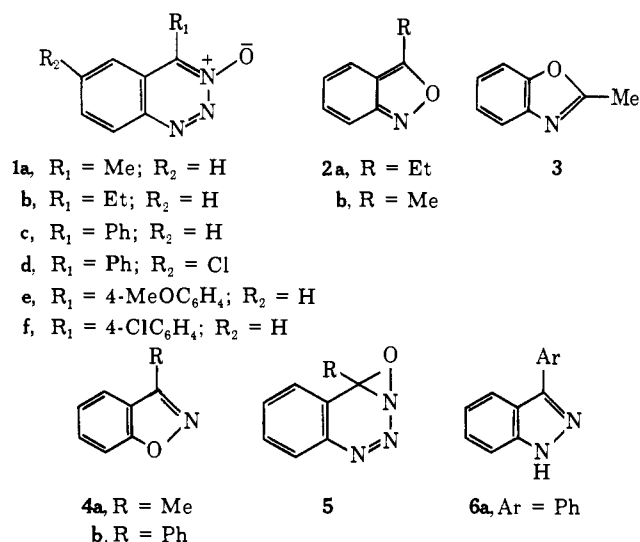
### Photolysis of 4-Substituted 1,2,3-Benzotriazine 3-N-Oxides

Sir:

Although the photolysis of many aromatic *N*-oxides has been extensively studied in recent years,<sup>1</sup> the 1,2,3-benzotriazine 3-*N*-oxides<sup>2</sup> have been overlooked. We report here the surprising results of their photolysis.

(1) G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970), and references cited therein.

(2) The ir, uv, nmr, and mass spectra of the 1,2,3-benzotriazine 3-*N*-oxides studied are only in agreement with the 1,2,3-benzotriazine 3-*N*-oxide structure.

4-Methyl-1,2,3-benzotriazine 3-*N*-oxide<sup>3</sup> (1a) and

its 4-ethyl analog<sup>4</sup> (**1b**) on irradiation<sup>5</sup> in methanol (ethanol or benzene) gave the 3-alkylanthranils (**2a** (95%) or **2b** (80%)), respectively and small amounts of the *o*-amino ketones (2-aminoacetophenone or 2-aminopropiophenone, respectively) (~5%).<sup>6</sup> Quantum yield measurements<sup>7</sup> (to 15% conversion) on the 4-methyl *N*-oxide ( $\lambda_{\max}$  in MeOH: 302 ( $\epsilon$  8200), 310 ( $\epsilon$  6800), 395 nm ( $\epsilon$  1200)) showed that anthranil formation ( $\phi_{\text{appearance}} = 0.13 \pm 0.02$ , for both  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  excitation)<sup>8</sup> was occurring at the same rate as *N*-oxide disappearance ( $\phi_{\text{disappearance}} = 0.13 \pm 0.01$ ). By analogy with the photolysis of other aromatic *N*-oxides,<sup>1</sup> the anthranil is possibly formed *via* the unstable oxaziridine intermediate (**5**). In cases where loss of nitrogen occurs on photolysis of aromatic *N*-oxides, oxaziridine intermediates have been postulated.<sup>9,10</sup>

However, when 4-phenyl-1,2,3-benzotriazine 3-*N*-oxide<sup>5</sup> (**1c**) was irradiated in methanol (ethanol or benzene), 3-phenylindazole (**6a**) (64%), 3-phenylbenzisoxazole (**4b**) (9%), and *o*-azidobenzophenone<sup>11</sup> were obtained on chromatography of the photolysis mixture. Similarly, the *N*-oxides (**1d-f**) gave indazoles in good yields. This is the first time that the loss of NO has been reported to occur on photolysis of an aromatic *N*-oxide. Quantum yield studies on (**1c**) ( $\lambda_{\max}$  in MeOH: 306 ( $\epsilon$  7100), 407 nm ( $\epsilon$  1700)) showed that the indazole ( $\phi_{\text{appearance}} = 0.03 \pm 0.01$ , for both  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  excitation)<sup>8</sup> is formed more slowly

(3) J. Meisenheimer, O. Senn, and P. Zimmermann, *Chem. Ber.*, **60**, 1736 (1927).

(4) New compounds reported in this communication were synthesized by standard procedures and had satisfactory analytical and spectral data.

(5) The light source was a 450-W medium-pressure mercury arc lamp. All irradiations were performed in Pyrex vessels. The solutions were deoxygenated by a nitrogen purge prior to and during photolysis.

(6) In some runs, 3-methylbenzoxazole (**3**, >3%) and 3-methylbenzisoxazole (**4a**, >3%) were also isolated from the photolysis of the 4-methyl *N*-oxide (**1a**).

(7) A grating monochromator with a 200-W super-pressure mercury arc was used. Actinometry, before and after irradiation, was carried out using ferrioxalate.

(8) The absorption at ~400-nm shifts to shorter wavelength in changing the solvent from cyclohexane to methanol and is assigned as  $n \rightarrow \pi^*$ : J. W. Sidman, *Chem. Rev.*, **58**, 689 (1958).

(9) O. Buchardt, *Tetrahedron Lett.*, 1911 (1968).

(10) T. Tsuchiya, H. Arai, and H. Igeta, *J. Chem. Soc., Chem. Commun.*, 550 (1972); *Tetrahedron Lett.*, 2579 (1971).

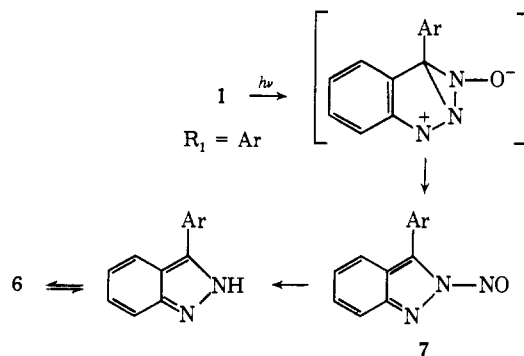
(11) *o*-Azidobenzophenone is formed when 4-phenyl-1,2,3-benzotriazine 3-*N*-oxide is subjected to column chromatography, heated, or treated with acid or base.

than the *N*-oxide ( $\phi_{\text{disappearance}} = 0.26 \pm 0.02$ ) decomposes. However, after leaving the photolyzed solutions for a few days, measurements for decomposition of *N*-oxide and formation of indazole were approximately the same. This clearly is due to the thermal decomposition of an intermediate produced photochemically. The thermal breakdown of this intermediate is enhanced by formic acid and sodium methoxide.

To account for the difference between this result, where NO is apparently extruded, and those normally encountered in *N*-oxide photolysis, formation of a bond between N-2 and C-4 is envisaged rather than the usual oxaziridine formation. The reaction scheme shown is one possible approach to this, producing an *N*-nitroso compound (**7**). Evidence for the formation of such an intermediate is obtained from the crude photolysis product of 4-phenyl-1,2,3-benzotriazine 3-*N*-oxide (**1c**) which gave a positive test for an *N*-nitroso compound (Liebermann's reaction). The enhanced decomposition of the intermediate, by addition of formic acid or sodium methoxide, is reasonable in view of the proposed structure, a 2-nitrosoindazole (**7**), considering that the presumably more stable 1-nitrosoindazoles are known to lose NO under acidic conditions.<sup>12</sup> The likely fate of the NO group in the presence of a carboxylic acid is the formation of an acyl nitrite. Acyl nitrites are reported to be diazotizing reagents.<sup>13</sup> The formation of such a compound was demonstrated by the production of 1-phenylazo-2-naphthol on irradiation (2 hr) of **1d** (0.5 g) in methanol (150 ml) with aniline (0.5 g), 2-naphthol (3 g), and formic acid (3 ml, 100%).

In summary we believe that 4-alkylbenzotriazine 3-*N*-oxides lose N<sub>2</sub> on photolysis while their 4-aryl analogs rearrange to 2-*N*-nitrosoindazoles which subsequently eliminate NO under action of solvent. Although the pathway by which the rearrangement takes place may be as indicated (Scheme I), the reason for

## Scheme I



the difference in reaction between the 4-alkyl and 4-aryl compounds is not known. Present work is aimed at a solution to this problem.

**Acknowledgement.** We thank the Science Research Council for financial support.

(12) F. Piozzi and M. Dubini, *Gazz. Chim. Ital.*, **89**, 638 (1959).

(13) V. V. Kozlov and B. I. Belov, *Zh. Obshch. Khim.*, **33**, 1951 (1963); *J. Gen. Chem. USSR*, **33**, 1898 (1963).

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