prior to irradiation and a slow stream of nitrogen was continued during photolysis. A Pyrex filter was placed between the light source and the reaction mixture.

After 6 hr, the solvent was removed by distillation *in vacuo* below 30°, producing a distillate which was transparent in the uv and leaving a yellow solid. The residual solid was chromatographed on an 85 × 2.5 cm silicic acid column slurry packed in 1:3 ether–hexane; 60-ml fractions were collected. The column was eluted as follows: 0.5 l. of 1:3 ether–hexane; 0.5 l. of 1:1 ether–hexane; 0.5 l. of 3:1 ether–hexane; and 0.5 l. of ether. Fractions 15–19 gave 175 mg of a pale yellow solid, mp 203–209°, recrystallized from ethanol–water to yield 164 mg of white crystals: mp 214–215° (the uv spectrum and the melting point of the photoproduct were identical with the reported spectrum[9] and melting point[10] for 11H-isoindolo[2,1-*a*]benzimidazole); nmr (CCl_4) τ 5.08 (s, 2) and 1.80–2.95 (m, 8). The identity of the photoproduct as 11H-isoindolo[2,1-*a*]benzimidazole (**5**) was confirmed by ir and mixture melting point comparison with an authentic sample[10] of **5**.

Test of the Stability of Benzo[3.4]cyclobuta[1,2-*b*]quinoxaline under Reaction and Isolation Conditions.—A control run in which 42 mg (0.21 mmol) of benzo[3.4]cyclobuta[1,2-*b*]quinoxaline (**2**) was subjected to the reaction and isolation conditions described in the previous experiment, except that no light was used, resulted in a quantitative recovery of starting material.

Pyrex-Filtered Irradiation of 11H-Isoindolo[2,1-*a*]benzimidazole (5) in Methanol.—11H-Isoindole[2,1-*a*]benzimidazole (**5**, 45 mg, 0.22 mmol) was irradiated in exactly the same manner as the irradiation of benzo[3.4]cyclobuta[1,2-*b*]quinoxaline (**2**). The isolation procedure was also the same. Fractions 14 and 15 from the chromatography column gave 30 mg of 11H-isoindolo[2,1-*a*]benzimidazole (**5**), mp 212–215°. No other compounds could be isolated. A stability test of **5** under reaction and isolation conditions but without the addition of light, similar to that described above for benzo[3.4]cyclobuta[1,2-*b*]quinoxaline (**2**), resulted in a quantitative recovery of **5**.

Registry No.—**2**, 259-57-4; **5**, 248-72-6.

[9] D. Amos and R. G. Gillis, *Aust. J. Chem.*, **17**, 1440 (1964).

[10] J. Thiele and K. G. Falk, *Justus Liebigs Ann. Chem.*, **347**, 114 (1906).

Deoxygenation of Benzoyl Cyanide[1]

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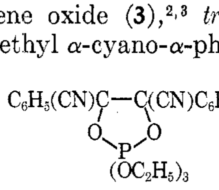
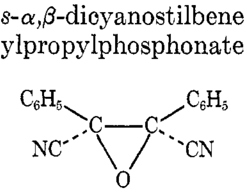
In refluxing benzene, triethyl phosphite and benzoyl cyanide (**1**) react over a period of 72 hr to form *cis*-α,β-dicyanostilbene oxide (**3**),[2,3] *trans*-α,β-dicyanostilbene (**4**),[2,3] and diethyl α-cyano-α-phenylpropylphosphonate (**5**). Intermediacy of a 1,3,2-dioxaphosph(V)olane **2**, a 2:1 adduct of starting materials which has been isolated when formed under milder conditions,[4,5] is assumed. Formation of **5** apparently requires an unprecedented 1,3 migration of an alkyl group from oxygen in a phosphonium ylide **8** to carbon.[6]

C_6H_5COCN

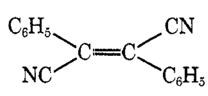
1



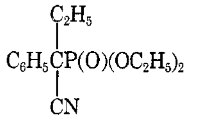
2



3

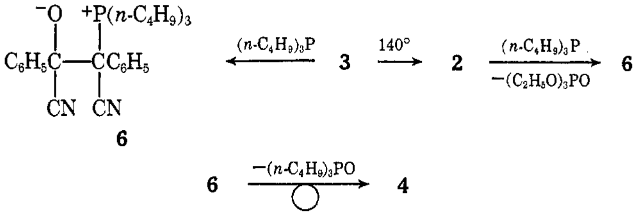


4

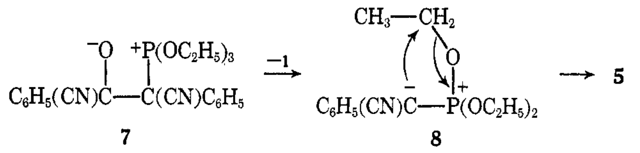


5

Thermal elimination of **3** from **2** and the transformation of both **2** and **3**, on treatment with tri-*n*-butylphosphine, into **4** have been reported.[4,5] From either starting material, **4** is presumably formed by an elimination with inversion[3] from the common intermediate zwitterion **6**.



A comparable zwitterion intermediate **7** is now assigned to the transformation of both **2** and **3** into **4** when each is treated with triethyl phosphite. By an alternative dissociation of **7**, benzoyl cyanide **1** and the phosphonium ylide **8** are available. The latter is isomeric with **5** and, although unprecedented, its proposed rearrangement by 1,3 migration of an ethyl group from oxygen to carbon accounts for the formation of **5**.[6] The rearrangement is reminiscent of the Arbuzov reaction in which a monoalkylphosphonic ester is formed upon heating a mixture of an alkyl halide and a trialkyl phosphite with an unstable phosphonium salt presumably as an intermediate.[7,8]



$$(RO)_3P \xrightarrow{R'X} (RO)_3\overset{+}{P}R'\ \overset{-}{X} \longrightarrow (RO)_2P(O)R' + RX$$

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[1] Financial support was received from NASA Grant No. NGR 14-012-004.

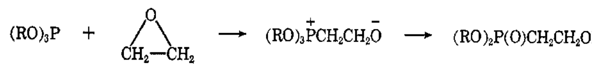
[2] J. H. Boyer and R. Selvarajan, Abstracts of 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, p S 111.

[3] C. J. Timmons and S. C. Wallwork [*Chem. Ind.* (London), 62 (1955)] conclusively established the configuration of *trans*-α,β-dicyanostilbene **4**, mp 161°, by X-ray analysis. M. V. Sargent and C. J. Timmons [*J. Chem. Soc.*, 2222 (1964)] established the configuration of *cis*-α,β-dicyanostilbene, mp 134°. Formation of **4**, in turn, provides a tentative *cis*-configurational assignment to **3**, since an inverted olefin is reported to predominate when an epoxide is deoxygenated by a tertiary phosphine [G. Wittig and W. Haag, *Chem. Ber.*, **88**, 1654 (1955); C. B. Scott, *J. Org. Chem.*, **22**, 1118 (1957); M. J. Boskin and D. B. Denney, *Chem. Ind.* (London), 330 (1959)].

[4] T. Mukaiyaka, I. Kuwajima, and K. Ohno, [*Bull. Chem. Soc. Jap.*, **38**, 1954 (1965)] incorrectly reversed the configurational assignments for **3** and **4**.

[5] P. C. Petrellis and G. W. Griffin [*Chem. Commun.*, 1099 (1968)] also observed the pyrolysis at 140° of **2** into **3**.[4]

[6] J. I. G. Cadogan [*Quart. Rev.*, **16**, 208 (1962)] discusses, p 216, a related reaction of epoxides with trialkyl phosphites which contain one or more secondary or tertiary alkyl groups. Phosphonates, rather than olefins and phosphates, are formed. An alkyl group migrates from oxygen to oxygen.



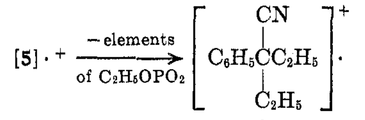
[7] R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 135–140.

[8] A. C. Poshkus and J. E. Herweh [*J. Org. Chem.*, **29**, 2567 (1964)] reported phosphonate formation by a related 1,3 migration of hydrogen in a reaction between benzophenone and triisopropyl phosphite.

$$(C_6H_5)_2CO + [(CH_3)_2CHO]_3P \longrightarrow (C_6H_5)_2C\overset{+}{P}[OCH(CH_3)_2]_3 / (C_6H_5)_2CO^- \longrightarrow (C_6H_5)_2CHP(O)[OCH(CH_3)_2]_2 + (C_6H_5)_2CO + CH_3CH{=}CH_2 + [(CH_3)_2CHO]_3PO$$

The ir spectrum of the phosphonate **5** shows strong $\overset{+}{P}—\overset{-}{O}$ and C≡N absorptions at 1255 and 2240 cm^{-1}, respectively. The nmr spectrum shows one quintet centered at δ 2.35, a second at 3.74, and a third at 4.20. Each quintet integrates for two protons. The two downfield absorptions are assigned to methylene groups attached to oxygen in agreement with reported nmr nonequivalence between methoxy[9a] and ethoxy[9b] groups attached to phosphorus. The upfield absorption at δ 2.35 is assigned to the protons of the methylene unit flanked by two carbon atoms. All six methylene protons exhibit long-range coupling with ^{31}P. By integration nine protons in methyl groups and five aromatic protons are observed.

A mass spectrometric analysis of the phosphonate **5** reveals a molecular ion (also the base peak) at *m/e* 281. An electron impact induced rearrangement accounts for the peak at *m/e* 173 assigned to the fragment molecular cation for phenyldiethylacetonitrile **9**. A similar electron impact induced 1,3 migration from oxygen to carbon has been reported for several other phosphonates.[10]

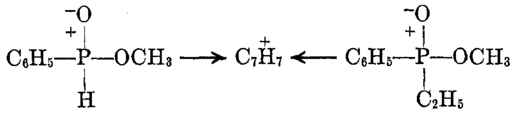


$$[\mathbf{5}]\cdot^{+} \xrightarrow[\text{of } C_2H_5OPO_2]{-\text{elements}} \left[\begin{matrix} CN \\ | \\ C_6H_5CC_2H_5 \\ | \\ C_2H_5 \end{matrix} \right]^{+}\cdot$$

9

$$C_6H_5CH_2P(O)(OC_6H_4R)_2 \longrightarrow C_6H_5\overset{+}{C}HC_6H_4R \quad \text{(ref 10)}$$

$$C_6H_5CH{=}CHP(O)(OC_2H_5)_2 \longrightarrow C_6H_5CH{=}CH\overset{+}{C}HCH_3 \quad \text{(ref 10)}$$



$$C_6H_5—\underset{H}{\overset{{}^{-}O}{\overset{+|}{P}}}—OCH_3 \longrightarrow C_7\overset{+}{H}_7 \longleftarrow C_6H_5—\underset{C_2H_5}{\overset{{}^{-}O}{\overset{+|}{P}}}—OCH_3 \quad \text{(ref 10)}$$

Experimental Section

A mixture of benzoyl cyanide (2.62 g, 20 mmol) and excess triethyl phosphite (13.2 g, 80 mmol) in anhydrous benzene (50 ml) was refluxed under nitrogen for 72 hr. From the reaction mixture the solvent was removed under vacuum; the residual liquid was distilled under vacuum giving a mixture of triethyl phosphite and triethyl phosphate, 9.6 g, bp 65–70° (1.25 mm). The pot residue was chromatographed over a column of silica (12 in. × 1 in.). The elutions with a 4:1 hexane–benzene mixture afforded colorless crystals of *cis*-α,β-dicyanostilbene oxide: 0.64 g, 26%; mp 166–166.5°; ir ($CHCl_3$) 2240 (w, CN), 1590 (w, aromatic), and 790 and 870 cm^{-1} (epoxide ring); λ_{max} (methanol) 222 mμ (ε 269.2) 278 (588.8) and 324 (933.3); nmr (CCl_4) multiplet centered at δ 7.58 (phenyl).

The elutions with hexane–benzene (3:1) gave colorless crystals of *trans*-α,β-dicyanostilbene: 0.53 g, 23%; mp 161.5–162° (benzene–hexane); ir ($CHCl_3$) 2230 (s, CN) and 1600 cm^{-1} (m, aromatic); λ_{max} ($CHCl_3$) 280 mμ (ε 3467) and 324 (15,490); nmr (CCl_4) multiplet centered at δ 7.65 (phenyl).

The elutions with benzene–ether (3:1) gave α-cyano-α-phenyl propyl phosphonate (1.0 g, 17.8%), a colorless viscous liquid which was further purified by distillation under vacuum (short path): bp 148–148.5° (0.75 mm); $n^{27.5}D$ 1.4955; ir (film) 2240 (m, CN), 1590 (w, aromatic), and 1255 cm^{-1} (vs, P=O); λ_{max} ($CHCl_3$) 312 mμ (ε 169.8); nmr (CCl_4) δ 0.92 (t, 3 H, $CC\mathbf{H}_3$), 1.02 (t, 3 H, $CC\mathbf{H}_3$), 1.40 (t, 3 H, $CC\mathbf{H}_3$), 2.35 (quintet, 2 H, $PCC\mathbf{H}_2CH_3$), 3.74 (quintet, 2 H, $POC\mathbf{H}_2CH_3$), 4.20 (quintet, 2 H, $POC\mathbf{H}_2CH_3$), and a multiplet centered at 7.50 (5 H, phenyl); mass spectrum *m/e* 281 (M^+) base peak, 266 $(M - CH_3)^+$, 253 $(M - C_2H_4)^+$, 238 $(M - CH_3 - C_2H_4)^+$, 255 $(M - 2C_2H_4)^+$, 210 $(M - CH_3 - 2C_2H_4)^+$, 197 $(M - 3C_2H_4)$, 173 $[C_6H_5(CN)C(C_2H_5)_2]^+$, 158 $[C_6H_5(CN)C(C_2H_5)CH_2]^+$, 145 $[C_6H_5HC(CN)C_2H_5]^+$, 144 $[C_6H_5C(CN)C_2H_5]^+$, 130 $[C_6H_5(CN)CHCH_2]^+$, 129 $[C_6H_5(CN)C{=}CH_2]$, 117 $(C_6H_5CH_2CN)^+$, 116 $(C_6H_5CHCN)^+$, 102 $(C_6H_5C{\equiv}CH)^+$, 91 $(C_7H_7)^+$, and 51 $(NCC{\equiv}CH)^+$.

Anal. Calcd for $C_{14}H_{20}NO_3P$: C, 59.78; H, 7.11; N, 4.98; P, 11.03. Found: C, 60.03; H, 7.14; N, 4.71; P, 10.69.

Registry No.—**1**, 613-90-1; **3**, 23214-43-9; **4**, 2450-55-7; **5**, 23230-35-5.

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(9) (a) F. Ramirez, A. V. Patwardhan, N. B. Desai, and S. R. Heller, *J. Amer. Chem. Soc.*, **87**, 549 (1965); (b) T. H. Siddall, III, and C. A. Prohaska, *ibid.*, **84**, 3467 (1962).

(10) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, p 649.

Lead(IV) Diacetate Difluoride. I. Reaction with Ketone Arylhydrazones[1]

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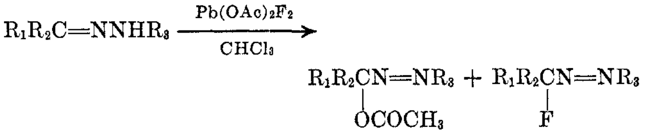
Recently, we reported the isolation of lead(IV) diacetate difluoride from the reaction of lead tetraacetate with liquid hydrogen fluoride in chloroform solution.[2] As part of a general study of the chemistry of this compound and because of a specific interest in its potential as a fluorinating agent, we have examined its action on a series of ketone arylhydrazones. It has been found that the reaction of lead(IV) diacetate difluoride with this class of compounds affords mixtures of azo acetates[3] and azo fluorides.[4] The former substances are well known and have been prepared by treatment of ketohydrazones[3] and ketazines[5] with lead tetraacetate; the azo fluorides, as far as we are aware, have not been prepared previously.



$$R_1R_2C{=}NNHR_3 \xrightarrow[CHCl_3]{Pb(OAc)_2F_2} \underset{OCOCH_3}{R_1R_2\overset{}{C}N}{=}NR_3 + \underset{F}{R_1R_2CN}{=}NR_3$$

The yields and properties of five azo fluorides and their accompanying azo acetates are summarized in Table I. Although the yields of the azo fluorides are smaller than those of the companion azo acetates, the mild conditions and ease of carrying out the reaction make this fluorination useful. Generally, the reaction was conducted under reflux in chloroform; at lower temperatures the yields of the azo fluorides were unchanged, but those of the azo acetates were substantially decreased in some cases. Resolution of the mixtures of azo compounds was trouble free and was readily effected either by column chromatography or by fractional distillation.

As shown in Table II, and in accordance with expectations, the ultraviolet spectra of the azo fluorides are

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(1) This research has been supported by National Science Foundation Grant GP-8672.

(2) J. Bornstein and L. Skarlos, *J. Amer. Chem. Soc.*, **90**, 5044 (1968).

(3) D. C. Iffland, L. Salisbury, and W. R. Schafer, *ibid.*, **83**, 749 (1961).

(4) For convenience and consistency, the term "azo fluoride" has been adopted for the general structure shown. See ref 3, footnote 3. The systematic fluoroarylazo alkane name is used throughout the text and Experimental Section.

(5) B. T. Gillis and M. P. La Montagne, *J. Org. Chem.*, **32**, 3318 (1967); **33**, 1294 (1968).