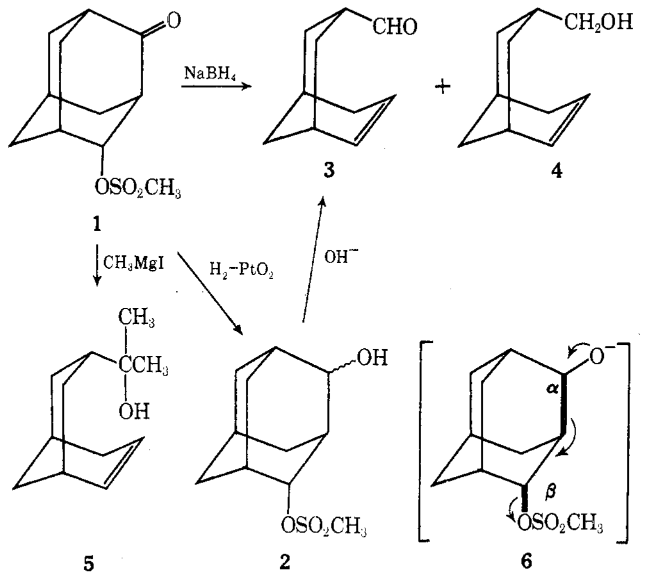
formation of **3** and **1** can be explained by an alkaline-induced ring fragmentation of the initially formed alcohol **2** as shown in Scheme I. In fact, treatment of **2** with ethanolic potassium hydroxide afforded aldehyde **3** in 60% yield. Alcohol **2** was easily obtained quantitatively as an oil by catalytic hydrogenation of **1** and had ir absorption bands (neat) at 3540, 3420, 1340 and 1185 $cm^{-1}$ and nmr ($CDCl_3$) signals at $\delta$ 5.08–4.88 (m, 1, $CHOSO_2$), 4.15–3.95 (m, 1, CHOH), 3.22 (s, $SO_2CH_3$), 2.62 (s, 1, OH), and 2.50–1.40 (m, 12, other ring protons).

SCHEME I



A further example of the facile ring cleavage of **1** was found in the reaction with Grignard reagent. Treatment of **1** with excess methylmagnesium iodide afforded alcohol **5**, mp 56–57°, in 75.5% yield, which was identified as bicyclo[3.3.1]non-6-ene-3-isopropyl alcohol by elemental analysis and direct comparison of spectral data and melting point with an authentic sample.[6]

The facile fragmentation aptitude of 2,4-disubstituted adamantanes can be understood in terms of the trans-coplanar geometry of the reacting bonds ($\alpha$ and $\beta$) in the intermediate as shown in **6**.[5,7] This is in good accordance with the results in the bicyclo[2.2.2]octane system reported recently by Kraus, *et al.*,[8] supporting the Grob hypothesis for fragmentation reactions.[9]

### Experimental Section[10]

**Reduction of 4(e)-Methylsulfonoxyadamantan-2-one (1) with Sodium Borohydride. Bicyclo[3.3.1]non-6-ene-3-aldehyde (3).**—To a stirred solution of **1** (0.40 g, 1.6 mmol) in methanol (30 ml) was added a solution of sodium borohydride (0.90 g, 2.3 mmol) in aqueous methanol (80% v/v, 25 ml) under ice cooling. After stirring was continued for 2 days at room temperature, the mixture was concentrated under reduced pressure in order to remove methanol, diluted with water, acidified with acetic acid, and extracted with ether (five 20-ml portions). The combined ether extracts were dried ($Na_2SO_4$), and the solvent was removed to give an oily residue which was purified on a silica gel (Mallinckrodt, 100 mesh) column eluting with chloroform. The first fraction gave **3** (0.13 g, 53%) as a colorless oil.

*Anal.* Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.00; H, 9.71.

Treatment of **3** with 2,4-dinitrophenylhydrazine gave the 2,4-DNP of **3** as red crystals from ethanol-chloroform: mp 210–211°; nmr ($CDCl_3$) $\delta$ 11.09 (s, 1, C=NNH), 9.29–8.00 (m, 3, phenyl protons), 7.62 (d, $J$ = 5.5 Hz, 1, CH=N), 6.05 (m, 2, CH=CH), and 2.70–1.40 (m, 11, remaining ring protons).

*Anal.* Calcd for $C_{16}H_{18}O_4N_4$: C, 58.17; H, 5.49; N, 16.96. Found: C, 58.13; H, 5.41; N, 16.84.

The second fraction gave alcohol **4** (0.10 g, 41%) as a colorless oil; the ir and nmr spectra and vpc retention time were identical with those of an authentic sample.[5]

**Catalytic Reduction of 1. 2-Hydroxy-4-methylsulfonoxyadamantane (2).**—A solution of **1** (1.0 g, 4.1 mmol) in methanol (20 ml) was hydrogenated in the presence of Adams catalyst (0.5 g) for 15 hr under atmospheric pressure at room temperature. After removal of the catalyst by filtration, the methanol solution was evaporated to dryness under reduced pressure to give **2** as an oil (0.99 g, 99%).

*Anal.* Calcd for $C_{11}H_{18}O_4S$: C, 53.63; H, 7.37. Found: C, 53.56; H, 7.43.

**Alkaline Cleavage of 2 to 3.**—Alcohol **2** (0.15 g, 0.61 mmol) was heated in 50% aqueous ethanol (8 ml) containing potassium hydroxide (0.20 g) at 60° for 6 hr. Work-up as usual afforded **3** in 60% yield.

**Reaction of 1 with Methylmagnesium Iodide. Bicyclo[3.3.1]-non-6-ene-3-isopropyl Alcohol (5).**—A solution of **1** (0.50 g, 2.1 mmol) in dry tetrahydrofuran (5 ml) was added to a solution of methylmagnesium iodide in tetrahydrofuran (15 ml) prepared from methyl iodide (2.5 ml) and magnesium (turnings, 1.1 g, 45.3 mg-atoms). After refluxing for 6.5 hr, the cooled reaction mixture was diluted with water (50 ml), acidified with 10% hydrochloric acid, and extracted with ether (four 40-ml portions). Work-up as usual afforded an oily product which was purified on a silica gel column eluting with chloroform to give **5** (0.28 g, 75.5%) as colorless crystals from *n*-hexane: mp 56–57° (lit.[6] mp 56.5–58°); ir (KBr) 3450, 3250, 3160, 1635, and 1140 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 6.00–5.10 (m, 2, CH=CH), 1.50 (s, 1, OH), 1.14 (s, 6, $OC(CH_3)_2$), and 2.50–0.60 (m, *ca.* 11, other ring protons).

*Anal.* Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.77; H, 11.35.

**Registry No.**—**2**, 31662-18-7; **3**, 31603-46-0; **3** DNP, 31603-47-1; **5**, 28644-53-3.

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[6] M. A. McKervey, D. Faulkner, and H. Hamill, *Tetrahedron Lett.*, 1971 (1970). Only the melting point is described herein.

[7] The fragmentation of homoadamantan-4-one systems does not seem to be as facile; *cf.* T. Sasaki, S. Eguchi, and T. Toru, *J. Org. Chem.*, **36**, 2454 (1971).

[8] W. Kraus and W. Rothenwohrer, *Tetrahedron Lett.*, 1007 (1968); W. Kraus and C. Chassin, *Justus Liebigs Ann. Chem.*, **735**, 198 (1970); W. Kraus and C. Chassin, *Tetrahedron Lett.*, 1003, 1113 (1970).

[9] C. A. Grob, *Angew. Chem.*, **81**, 543 (1969); C. A. Grob and P. W. Schiess, *ibid.*, **79**, 1 (1967).

[10] *Cf.* footnote 27 in ref 5.

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## Tricarbethoxyphosphine

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As part of a program on the synthesis of new flame retardants for cotton, we were interested in preparing the tertiary phosphine containing three carboxamide substituents directly attached to phosphorus, $P(CONH_2)_3$. This compound, which is unknown, was to be prepared by ammonolysis of the corresponding triester, $P(CO_2Et)_3$ (I). Tertiary phosphines which contain one or two carbethoxy substituents are known,[2,3] but the triester I has not been described in the literature.

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[1] One of the laboratories of the Southern Marketing and Nutrition Research Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] A. Job and G. Dusollier, *C. R. Acad. Sci.*, **184**, 1454 (1927).

[3] K. Issleib and H. Anhöck, *Z. Naturforsch. B*, **16**, 837 (1961).

Tricarbethoxyphosphine (I) was prepared in 29% yield by the reaction of ethyl chloroformate with $Na_3P$.

$$\mathrm{Na_3P + 3ClCO_2R \longrightarrow P(CO_2R)_3 + 3NaCl}$$
$$\begin{array}{l}\mathrm{I,\ R = Et}\\ \mathrm{II,\ R = Bu}\\ \mathrm{III,\ R = Ph}\end{array}$$

The reaction stopped at the tertiary phosphine stage, despite the use of excess ethyl chloroformate. Alkyl chloroformates, unlike alkyl halides, do not quaternize tertiary phosphines, but tend to be decomposed by them with loss of $CO_2$.[4]

The yield, though low, represented the best of several trials. The most important variable was found to be the source of the trisodium phosphide, best results being obtained with the product of the reaction of white phosphorus with the green sodium–naphthalene radical anion in tetrahydrofuran.[5] Slightly lower yields (20–26%) were obtained with red phosphorus, which was safer but slower, but, when the $Na_3P$ was prepared by the reaction of phosphorus trichloride[6] or white phosphorus[7] with sodium dispersed in toluene, no I was obtained at all, even though the ethyl chloroformate appeared to react.[8] The blue sodium–anthracene radical anion[9] gave a 23% yield of I, contaminated with 9,10-dihydroanthracene.[10]

Alternate routes, such as the reaction of ethyl chloroformate with the magnesium phosphide[11] $P(MgCl)_3$, or with phosphine in the presence of a tertiary amine such as triethylamine or dimethylaniline,[12] also failed to give any I.[13,14]

I was a colorless, mobile, air-stable liquid with a characteristic, sweet odor. It was soluble in organic solvents and insoluble in water. It gave no color reaction with carbon disulfide (in which it was insoluble), nor with benzoquinone nor benzofuroxan,[15,16] all characteristic tests for tertiary phosphines. It was recovered unchanged after 4 days with methyl iodide in tetrahydrofuran, and after treatment with aniline[17] or sulfur in boiling xylene.

In view of this demonstrated lack of reactivity, we were surprised to find that I instantly decolorized bromine in $CCl_4$ (or ethanol), and could be titrated quantitatively with this reagent. One mole of bromine was consumed per mole of I.[18]

Hydrolysis of I with 1 *N* NaOH took place rapidly at 100°, expelling phosphine.[19]

$$\mathrm{P(CO_2Et)_3 + 6NaOH \longrightarrow PH_3 + 3Na_2CO_3 + 3EtOH}$$

After 3 hr at 100°, the reaction yielded 81.5% of phosphine and 86.5% of sodium carbonate. Under similar conditions, hydrolysis with 1 *N* HCl generated only 23% of phosphine.

Oxidation of I with 30% hydrogen peroxide took an unusual and unexpected course. Instead of the tertiary phosphine oxide, $O{=}P(CO_2Et)_3$, the reaction gave a 1:1 mixture of phosphorous acid and hypophosphorous acid. We could find no precedent for this in the literature. Hypophosphorous acid might be formed by a two-step sequence involving oxidation and hydrolysis.

$$\mathrm{P(CO_2Et)_3 + H_2O_2 \longrightarrow HOP(O)(CO_2Et)_2 + HCO_2Et}$$
$$\mathrm{HOP(O)(CO_2Et)_2 + 2H_2O \longrightarrow H_3PO_2 + 2EtOH + 2CO_2}$$

Further oxidation of the hypophosphorous acid by the 0.5 *M* excess of hydrogen peroxide used in the reaction would account for the presence of phosphorous acid in the reaction mixture. No formic acid was detected.[20]

Oxidation was even more vigorous when a base, sodium carbonate, was added to the reaction mixture. One mole of carbon dioxide was evolved for each mole of hydrogen peroxide employed.

The phosphine I also appeared to be destroyed by other oxidant systems, such as permanganate in acetone or bromine in ethanol.[21] The latter gave a 36% yield of an ester of phosphorous acid, *viz.* diethyl phosphonate, as one reaction product.

Mercuric chloride in ethanol was reduced by I to mercurous chloride (86%) after 5-hr refluxing, leaving an acidic residue. The Hg(II) salt, which often forms crystalline complexes with tertiary phosphines, functioned in this instance simply as a halogenating agent.

The reaction of I with ammonia in ethanol solution gave urea (91.5%) and an unstable oil, $n^{20}\mathrm{D}$ 1.4764, which deposited an amorphous yellow solid on standing. The ir spectrum of the oil showed ester C–H and amide N–H bands but no P–H nor P–OH bands.[22] The oil and the yellow solid were not identified, but it is obvious that neither substance was the carboxamide, $P(CONH_2)_3$.

The results[23−27] of these experiments are assembled in

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[4] H. J. Bestmann and K. H. Schnabel, *Justus Liebigs Ann. Chem.*, **698**, 106 (1966).

[5] D. J. Peterson, U. S. Patent 3,397,039 (Aug 13, 1968). We are indebted to Dr. T. J. Logan of the Procter & Gamble Co., Cincinnati, Ohio, for bringing this patent to our attention.

[6] L. Horner, P. Beck, and H. Hoffmann, *Chem. Ber.*, **92**, 2088 (1959).

[7] D. J. Peterson and T. J. Logan, *J. Inorg. Nucl. Chem.*, **28**, 53 (1966).

[8] The $Na_3P$ prepared by the high-speed stirrer methods[6,7] appeared to be very finely divided, whereas the products of the radical anion routes were granular. All were black, including the $PCl_3$ product,[6] which contained 3 mol of NaCl.

[9] D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Amer. Chem. Soc.*, **78**, 116 (1956).

[10] The carrier anthracene (or naphthalene) is usually regenerated when the $Na_3P$ is formed, but in this experiment 5.1% of the 9,10-dihydro derivative, mp 107–108°, was isolated as a by-product.

[11] L. Horner and H. Hoffmann, "Newer Methods of Preparative Organic Chemistry," Vol. II, W. Foerst, Ed., Academic Press, New York, N. Y., 1963, p 208.

[12] Ethyl chloroformate reacts vigorously with pyridine or triethylamine but not with dimethylaniline, not even when heated.

[13] The salt $[Et_3NCO_2Et]Cl$, obtained as a thick slurry in ether at ice-bath temperature,[14] was slowly decomposed by phosphine at room temperature giving 15% of triethylamine hydrochloride, mp 254–255°, as the only nonvolatile product.

[14] M. Matzner, R. P. Kurkjy, and R. C. Cotter, *Chem. Rev.*, **64**, 645 (1964).

[15] A. S. Bailey, J. M. Peach, C. K. Prout, and T. S. Cameron, *J. Chem. Soc. C*, 2277 (1969).

[16] J. H. Boyer and S. E. Ellzey, Jr., *J. Org. Chem.*, **26**, 4684 (1961).

[17] In an attempt to prepare the known compound $P(CONHPh)_3$, mp 212–213°: S. A. Buckler, *ibid.*, **24**, 1460 (1959).

[18] Triphenylphosphine, in contrast, cannot be titrated with bromine in $CCl_4$, as it consumes much more than the amount required for the formation of the 1:1 adduct $Ph_3PBr_2$.

[19] The components $R_2PCO_2Et$ (R = Et, Ph, $C_6H_{11}$) similarly yield $R_2PH$ upon hydrolysis with alkali.[3]

[20] The occurrence of ethyl formate as one of the reaction products seems to be required by the stoichiometry. There was not enough hydrogen peroxide present for the reaction $\mathrm{P(CO_2Et)_3 + 2H_2O_2 + H_2O \rightarrow H_3PO_2 + 3EtOH + 3CO_2}$.

[21] A. W. Frank and C. F. Baranauckas, *J. Org. Chem.*, **31**, 872 (1966).

[22] Ir (neat, taken at once) 1070 s, 1098 m, 1175 m br, 1335 s, 1377 s, 1412 m, 1450 w, 1470 w, 1610 m, 1670 m, 1720 vs (C=O), 3000 w (CH), 3225 w (NH), 3380 s (NH), 3500 s cm$^{-1}$ (NH).

[23] W. E. White and A. H. Bushey, *J. Amer. Chem. Soc.*, **66**, 1966 (1944).

[24] D. A. Skoog and D. M. West, "Fundamentals of Analytical Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1966, p 352.

[25] A. I. Vogel, "A Textbook of Macro and Semimicro Qualitative Inorganic Analysis," 4th ed, Longmans, Green and Co., London, 1954, p 392.

[26] P. Lemoult, *C. R. Acad. Sci.*, **142**, 1193 (1906).

[27] A. E. Arbuzov and B. A. Arbuzov, *J. Prakt. Chem.*, [2] **130**, 103 (1931).

Table I. In retrospect, it appeared that I was reactive only toward reagents which affected the ester groups (with the exception of bromine), suggesting a very low order of nucelophilicity for the phosphorus atom. To obtain a measure of the basicity of I, a measurement was made of the shift of the OD peak of methanol-*d* induced by I in the infrared spectrum of a solution of $CH_3OD$ in $CCl_4$. From this measurement, the p$K_a$ of I was calculated[28] to be −10.9, an exceedingly low figure. The tributyl ester II gave a similar figure, p$K_a$ = −10.4.

TABLE I

SUMMARY OF REACTIONS WITH I

| Reagent | Solvent | Conditions | Products (% yield) |
|---|---|---|---|
| NaOH | $H_2O$ | 100°, 3 hr | $PH_3$ (81.5),[a] $Na_2CO_3$ (86.5)[b] |
| HCl | $H_2O$ | 100°, 3 hr | $PH_3$ (23),[a] I (28) |
| $H_2O_2$ | Acetone | RT, 15 min | $H_3PO_2$ (42.4), $H_3PO_3$ (45.5)[c] |
| $H_2O_2(Na_2CO_3)$ | Acetone | RT,[d] 15 min | $NaHCO_3$ (89)[b] |
| $Br_2$ | EtOH | 0–10°, 5 min | $(EtO)_2P(O)H$ (36)[e] |
| $HgCl_2$ | EtOH | 78°, 5 hr | $Hg_2Cl_2$ (86) |
| $NH_3$ | EtOH | RT,[f] 30 min | Urea (91.5)[g] |

[a] Analyzed by the $HgCl_2$ method;[23] bromphenol blue was found to be a useful indicator for this titration. [b] Analyzed by the Winkler method.[24] [c] By titration with 0.1 *N* NaOH. $H_3PO_2$ confirmed by tests with copper sulfate and potassium permanganate,[25] and $H_3PO_3$ by precipitation as the aniline salt, mp 167–169° (lit.[26] mp 179°); $H_3PO_4$ absent. [d] Exotherm to 56°. [e] Bp 47° (0.2 mm), $n^{20}_{\mathrm{D}}$ 1.4560 [lit.[27] bp 51–52° (2 mm), $n^{20}_{\mathrm{D}}$ 1.4082]. Refractive index high because sample contained naphthalene (ir). [f] Exotherm to 40°. [g] Mp 132–133°, confirmed as urea by ir and biuret test.

Calculation of the base strength of the tertiary phosphine $P(CO_2Me)_3$, using the appropriate Henderson–Streuli equation[29] and Taft substituent constant,[30] gives a p$K_a$ of −8.17 for this ester. The actual values for I and II were somewhat lower than this, but within the limits of accuracy of method (p$K_a$ = ±2). Normal p$K_a$ values for tertiary phosphines, $R_3P$, are in the 8–9 range, *e.g.*, 8.69 for R = Et, but extend as low as 2.73 for R = Ph and 1.36 for R = $CH_2CH_2CN$.[29]

Two other phosphine triesters were prepared by the reaction of trisodium phosphide with the appropriate chloroformate ester. The tributyl ester $P(CO_2Bu)_3$ (II), bp 147° (0.2 mm), was prepared in 27% yield by the reaction of trisodium phosphide with butyl chloroformate, and the triphenyl ester, $P(CO_2Ph)_3$ (III), mp 125–126°, in 7% yield, together with 22% of diphenyl carbonate, by the reaction of trisodium phosphide with phenyl chloroformate. Methyl chloroformate decomposed on contact with the phosphide.

## Experimental Section[31]

**Starting Materials.**—Commercial reagents were generally used without further purification. The tetrahydrofuran (Eastman White Label)[32] used in the first preparation of I was dried over KOH and distilled from lithium aluminum hydride. Later, it was discovered that the green sodium–naphthalene radical anion was formed in less than 5 min even when the solvent was not purified. The stabilizer (0.025% BHT) in the solvent evidently did not interfere. The solvent was used thereafter as obtained.

**Tricarbethoxyphosphine** (I).—Ethyl chloroformate (21.7 g, 0.2 mol) was added dropwise to a well-stirred slurry of trisodium phosphide[5] (4.0 g, 0.04 mol) in tetrahydrofuran (100 ml), with ice-cooling applied as necessary to moderate the mild exotherm. The mixture was then heated briefly to reflux, allowed to cool to room temperature, and treated cautiously with anhydrous ethanol (25 ml) to decompose any excess Na or $Na_3P$. The mixture was filtered under vacuum through a fine, fritted-glass filter (very slow), giving 7.5 g of yellow, malodorous, water-insoluble solid,[33] and a filtrate which, when concentrated, left 9.4 g of yellow liquid. A Beilstein test for Cl on the liquid was negative, but the liquid still contained the naphthalene (1.5 g) which had been used in the preparation of the $Na_3P$.[5] The naphthalene was removed by distillation at 130° bath temperature (1.0 mm), the apparatus being disassembled and cleaned several times until no more naphthalene distilled.[34] The product was then distilled, giving 2.9 g (29%) of I, bp 130° (1.0 mm), $n^{20}_{\mathrm{D}}$ 1.4678, as a colorless, mobile liquid with a sweet odor: ir (neat) 777 w, 848 m, 1010 s, 1095 sh, 1135 vs, 1175 vs, 1210 s, 1290 w, 1360 w, 1385 w, 1445 w, 1465 w, 1730 vs (C=O), 3000 m cm$^{-1}$ (CH); nmr (neat) $\delta$ 1.28 (t, 9 H, $CH_3$, $J$ = 7.0 Hz), 4.28 ppm (q, 6 H, $CH_2$, $J$ = 7.0 Hz); $^{31}$P $\delta$ −3.37 ppm.

*Anal.* Calcd for $C_9H_{15}O_6P$: C, 43.20; H, 6.04. Found: C, 43.44; H, 6.14.

The compound was soluble in ethanol, benzene, $CCl_4$, and THF, but insoluble in water.

The preparation was repeated on a 15-fold scale, giving 64.4 g (26%) of I, bp 129–131° (1.4 mm). On this scale, filtration of the reaction mixture would have been tedious. Fortunately, it was discovered that the reaction mixture could be partitioned between benzene and water, despite the presence of large volumes of ethanol (250 ml) and THF (2500 ml). The reaction mixture was diluted with an equal volume of water and extracted three times with benzene, giving 244.1 g of a dark red oil from which I was obtained by distillation.

**Titration of I with Bromine.**—A 0.259-g sample of I in 5 ml of $CCl_4$ was titrated rapidly with 0.135 *M* $Br_2$ in $CCl_4$ to a permanent yellow end point. The phosphine consumed 7.80 ml of the bromine reagent, corresponding to 1.02 mol of $Br_2$ per mole of I.

I also decolorized $I_2$ in $CCl_4$, but not $I_2$ in benzene.

**Tris(butoxycarbonyl)phosphine** (II).—The reaction of 47.8 g (0.35 mol) of butyl chloroformate with 10.0 g (0.1 mol) of trisodium phosphide in 250 ml of tetrahydrofuran gave 17.1 g of distilled product which, when redistilled, gave fractions (a) 0.8 g, bp 110–147° (0.2 mm), $n^{20}_{\mathrm{D}}$ 1.4602; (b) 4.7 g, bp 147° (0.2 mm), $n^{20}_{\mathrm{D}}$ 1.4646; and (c) 8.2 g, bp 147–149° (0.2 mm), $n^{20}_{\mathrm{D}}$ 1.4668. The yield of II was 12.9 g (27%). Fraction b data: ir (neat) 738 w, 790 w, 830 w, 900 w, 926 m, 960 w, 990 w, 1012 w, 1055 w, 1135 vs, 1200 s, 1235 m, 1375 w, 1465 m, 1725 vs (C=O) and 2970 cm$^{-1}$ (CH); $^1$H nmr ($CDCl_3$),[35] $\delta$ 0.93 (t, 9 H, $CH_3$, $J$ = 7.0 Hz), 1.1–1.9 (m, 12 H, $CH_2CH_2CH_3$), and 4.33 ppm (t, 6 H, $OCH_2$, $J$ = 6.5 Hz); $^{31}$P nmr (neat) $\delta$ −3.85 ppm.

*Anal.* Calcd for $C_{15}H_{27}O_6P$: C, 53.88; H, 8.14; P, 9.27. Found: C, 54.01; H, 8.27; P, 9.29.

**Tris(phenoxycarbonyl)phosphine** (III).—The reaction of 54.8 g (0.3 mol) of phenyl chloroformate with 10.0 g (0.1 mol) of trisodium phosphide in 300 ml of tetrahydrofuran gave, after stripping off the naphthalene and some volatile liquid at 130° (0.5 mm), an oil which solidified on cooling to a hard mass of crystals (33.4 g). The crude product was taken up in a large volume (500 ml) of warm ethanol and filtered, giving 9.0 g of dark yellow, amorphous solid (discarded). The filtrate was concentrated and recrystallized once from ethanol, giving 2.75 g (7%) of III:

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(28) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

(29) W. A. Henderson, Jr., and C. A. Streuli, *J. Amer. Chem. Soc.*, **82**, 5791 (1960).

(30) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 619.

(31) Melting points are corrected. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra, with the exception of those used for the basicity measurements, were taken on a Perkin-Elmer Model 137B instrument with NaCl optics. $^1$H nmr spectra were taken on a Varian A-60 spectrometer using TMS as internal standard, and $^{31}$P nmr on a Varian HA-60-IL instrument at 24.3 Mcps, using 85% $H_3PO_4$ as external standard.

(32) Naming of firms or their products in this paper does not imply their endorsement by the Department of Agriculture.

(33) In subsequent runs the solid was mixed with Filter-aid to aid in its removal. Its color varied from yellow to olive-brown.

(34) Naphthalene was easily detected in the product by its ir absorption at 788 cm$^{-1}$.

(35) This spectrum bore a striking resemblance to that of dibutyl carbonate, in "High Resolution NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, No. 243.

pale yellow needles; mp 125–126°; ir (Nujol) 686 s, 740 vs, 794 m, 833 w, 848 m, 918 m, 1002 m, 1022 m, 1105 vs, 1160 s, 1176 s, 1486 m, 1587 w (C═C aromatic) and 1733 cm$^{-1}$ (C═O); nmr (CDCl$_3$) δ 7.35 ppm (m).

*Anal.* Calcd for $C_{21}H_{15}O_6P$: C, 63.96; H, 3.85; P, 7.86. Found: C, 63.48; H, 4.14; P, 7.67.

III is soluble in benzene and in warm methanol and insoluble in water or carbon tetrachloride.

The mother liquor from the recrystallization of III was concentrated to low volume, filtered, and evaporated to dryness, giving 7.05 g (22%) of pale yellow, crystalline solid, mp 70–72°, identified by its ir spectrum as impure diphenyl carbonate. The melting point was raised to 76.5–77.5° (lit.[36] mp 79°) by recrystallization from methanol–water.

*Anal.* Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71. Found: C, 71.43; H, 4.56; P, 0.86.

The phenyl chloroformate used in this reaction did not contain any diphenyl carbonate (ir). The diphenyl carbonate is therefore a by-product of the reaction with $Na_3P$.

**Basicity Measurements.**—The base strengths of I and II were determined by the MeOD method,[28] using 0.5 mm cells and a grating instrument (Perkin-Elmer 421) calibrated with polystyrene. The spectra were scanned from 2800 to 2200 cm$^{-1}$. A 0.25 *M* solution of MeOD in CCl$_4$ showed a strong, sharp peak at 2680 cm$^{-1}$ ($\nu_{OD}$ free) and a strong, broad peak at 2482 cm$^{-1}$ ($\nu_{OD}$ bonded, owing to self-association of the MeOD). Upon the addition of a base (1.0 *M*), the 2680-cm$^{-1}$ peak diminished in intensity and the 2482-cm$^{-1}$ peak shifted and became stronger. Observed shifts for various bases, relative to the 2680-cm$^{-1}$ peak, were $\Delta\nu$ 120 (DMF), 100 (dioxane, lit.[28] 111), 65 (CH$_3$CN, lit.[28] 63), 35 (I), and 40 cm$^{-1}$ (II).

Using the data, and the expression $pK_a = 0.1[\Delta\nu] - 14.4$ derived from Arnett's Figure 5,[28] the base strengths of I and II were calculated to be $pK_a = -10.9$ and $-10.4$, respectively.

The phenyl ester III was not sufficiently soluble in CCl$_4$ to obtain a measurement.

**Registry No.**—I, 31081-90-0; II, 31128-88-8; III, 31128-89-9.

**Acknowledtments.**—We are indebted to Dr. R. H. Dinius, Auburn University, for the $^{31}$P nmr spectra, and to Mr. G. J. Boudreaux and Miss E. R. McCall of this Laboratory for the $^1$H nmr spectra and ir basicity measurements, respectively.

[36] P. D. Ritchie, *J. Chem. Soc.*, 1054 (1935).

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# Photolysis and Pyrolysis of 2-Azido-3-nitronaphthalene

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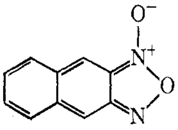
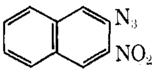
To test the formation of an apparently unfavorable quinonoid system contained in naphtho[2,3-*c*]furoxan (**1**), the expulsion of nitrogen from 2-azido-3-nitronaphthalene (**2**) has been investigated.[1,2] As expected, both irradiation and heat bring about the release of molecular nitrogen; however, neither the furoxan nor its isomer, 2,3-dinitrosonaphthalene (**3**), could be detected.

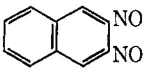
Consideration of the greater thermal stability of 5-nitro- and 8-nitro-2-azidonaphthalene[3] over 1-nitro-2-azidonaphthalene and the isomer **2** provides an explanation for an increased facility in the release of nitrogen from **2** through anchimeric assistance by the adjacent nitro group. In the present instance, no products in which a new NO bond is formed were isolated. The reaction apparently leads to the intermediate 3-nitronapthyl-2-nitrene (**4**). Hydrogen abstraction from the solvent with the formation of 2-amino-3-nitronaphthalene (**5**) in both thermal and photoelimination reactions is diagnostic of the nitrene intermediate. The additional photogeneration of 3,3′-dinitro-2,2′-azonaphthalene (**6**) is best accounted for by interaction between the azide **2** and the nitrene **4**.



**1**



**2**



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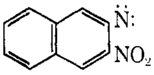
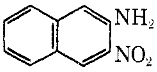
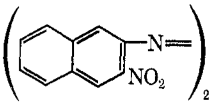


**4**



**5**



**6**

## Experimental Section[4]

After nitrogen was flushed through a solution of the azide **2** (200 mg, 0.93 mmol) in anhydrous benzene for 16 hr, it was irradiated with 254-nm low-pressure mercury lamps in a Rayonet chamber reactor and the reaction was monitored by ir. After 1.5 hr of irradiation the solution was concentrated under vacuum (60°). The residue was triturated with benzene (10 ml), filtered, and twice recrystallized from nitromethane as red needles of 2,2′-dinitroazonaphthalene (33 mg, 18.5%): mp 365–370° dec; ν max (KBr) 1520 and 1340 cm$^{-1}$ (NO$_2$); mass spectrum *m/e* 372 (M$^+$, parent peak), 356 (M − O)$^+$, 340 (M − O$_2$)$^+$, 310 (M − NO$_2$ − O)$^+$, 200 (M − $C_{10}H_6NO_2$)$^+$, 144 ($C_9H_6NO$)$^+$, 114 ($C_9H_6$)$^+$, and 57 ($C_9H_6$)$^{2+}$; $\lambda_{max}$ (CHCl$_3$) 290 nm (ε 38,370) and 390 (17,740).

*Anal.* Calcd for $C_{20}H_{12}N_4O_4$: C, 64.52; H, 3.22; N, 15.06; mol wt, 372. Found: C, 64.46; H, 3.18; N, 15.27.

The benzene filtrate was concentrated and the residual solid was purified by chromatography over a column of silica gel (10 × 1 in.). Elutions with a 1:1 hexane–benzene mixture (450 ml) gave 2-azido-3-nitronaphthalene (6 mg, 3%), mp and mmp (with an authentic sample) 101–102°. Subsequent elutions with the same solvent mixture (600 ml) and a 1:2 mixture (300 ml) gave a red residue. It was treated with Norit in benzene and recrystallized from hexane as microscopic red needles of 2-amino-3-nitronaphthalene (8.5 mg, 4.5%): mp and mmp (with the authentic sample) 108–109°; ir (KBr) superposable with the authentic spectrum. Further elutions with polar solvents afforded an intractable resinous product.

A solution of the azide (200 mg, 0.94 mmol) in anhydrous octane (10 ml) was heated at 100° with stirring for 8 hr while the reaction was monitored by tlc. From the dark reaction mixture the solvent was removed under vacuum [50° (25 mm)]. The residue upon tlc examination, using ChromAR-500 sheets with benzene and ethyl acetate solvents, indicated the presence of the unreacted 2-azido-3-nitronaphthalene and 2-amino-3-nitronaphthalene. The residue was purified by chromatography

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[1] A. Rahman, A. J. Boulton, D. P. Clifford, and G. J. T. Tiddy, *J. Chem. Soc. B*, 1516 (1968), reported stability of the azide **2** which is inconsistent with the present observations.

[2] The azide was prepared from 2,3-dinitronaphthalene.[1] A sample of this dinitro derivative was obtained from the Fundamental Research Company, Berkeley, Calif.

[3] M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **91**, 1942 (1907), reported 5-nitro-2-azidonaphthalene, mp 133.5° (no decomposition) and stability in boiling glacial acetic acid; 8-nitro-2-azidonaphthalene, mp 108° (no decomposition); 1-nitro-2-azidonaphthalene, mp 116–117° (vigorous decomposition) and slow evolution of nitrogen when heated in ethanol.

[4] Microanalyses by Micro-Tech Laboratories, Skokie, Ill. Instrumental data were obtained from a Perkin-Elmer 237-B infrared spectrophotometer, a Cary-14 ultraviolet spectrometer, a Perkin-Elmer 270 mass spectrometer, a Varian Aerograph 1800 gas chromatograph, and a Reichert microscope melting point apparatus.