Table II. Aldehydes Treated with Hydrogen over Borohydride-Reduced Nickel[a]

Registry no.	Reactant	Product	Ni, mmol	Time,[b] h
107-02-8	Acrolein	Propionaldehyde	5	0.5
4170-30-3	Crotonaldehyde	Butyraldehyde	5	8
	Crotonaldehyde	Butyraldehyde	20	0.75
104-55-2	Cinnamaldehyde	Hydrocinnamaldehyde	20	1
497-03-0	Tiglaldehyde	α-Methylbutyraldehyde	20	1
123-38-6	Propionaldehyde	Propyl alcohol	50	15
123-72-8	Butyraldehyde	Butyl alcohol	50	21
104-53-0	Hydrocinnamaldehyde	3-Phenylpropanol	20	4
96-17-3	α-Methylbutyraldehyde	2-Methylbutanol	20	7.5
100-52-7	Benzaldehyde	Benzyl alcohol	10	48
98-01-1	Furfural	Furfuryl alcohol	5	12

[a] 100 mmol of reactant, 30 psi initial H_2 pressure, ambient temperature, in 50 ml of 95% ethanol. [b] Hours for uptake of 100 mmol of H_2.

Table III. Hydrogenation Times for Crotonaldehyde in Various Solvents[a]

Solvent	Time,[b] min
Cyclohexane	35
1,2-Dimethoxyethane	20
Dimethylformamide[c]	55
Methanol	15
Toluene	40

[a] 100 mmol of reactant, 2.5 mmol of Pd, 40 ml of solvent, 30 psi H_2 initial pressure, ambient temperature. [b] Minutes for uptake of 100 mmol of H_2. [c] Catalyst prepared in methanol. Black material prepared in DMF did not effect hydrogenation in DMF.

lower grade chemicals and were used directly from the bottles without further purification. Palladium chloride was from Research Organic Chemicals; nickel acetate was from Fisher Scientific. All organic chemicals were analyzed for purity by gas chromatography prior to use. Liquid phases for GC analyses included XF-1150, SE-30, QF-10065, Carbowax 20M, and SF-96.

Catalyst Preparation. Nickel. To a stirred suspension of 1.24 g (5 mmol) of powdered nickel acetate in 50 ml of 95% ethanol was added 5 ml of 1.0 M sodium borohydride in 95% ethanol at room temperature. (Other amounts of catalyst were prepared by using multiples of the amounts of reactants.) Stirring was continued until the evolution of a gas had ceased, usually within 30 min. The black colloidal material was used directly.

Palladium. To a stirred suspension of 0.443 g (2.5 mmol) of powdered palladium chloride in 40 ml of absolute methanol, or other liquid, at room temperature was added 0.19 g (5 mmol) of powdered sodium borohydride over a 5–10-min period. (Other amounts of the catalyst were prepared by using multiples of the amounts of reactants.) Stirring was continued until the evolution of a gas had ceased, usually within 20 min. The black catalyst settled rapidly when stirring was stopped. The solvent is changed readily by decanting and washing two or three times.

Hydrogenation Procedure. To the desired amount of catalyst and solvent in a hydrogenation flask was added 100 mmol of purified aldehyde. The flask was flushed with hydrogen, connected to a Parr low-pressure hydrogenator, and pressurized to 30 psi. Time and pressure were monitored. Reactions were begun at room temperature and conducted under ambient conditions.

The nickel catalyst was removed by centrifugation prior to product analysis. The palladium catalyst settled rapidly upon cessation of shaking.

Product Analysis. Infrared spectra of reaction mixtures were taken prior to gas chromatographic analyses to enable detection of unexpected thermal reactions and incomplete elutions. All reaction mixtures were analyzed directly, after removal of the catalyst, with the exception of those in dimethylformamide. These reaction mixtures were extracted with water and ethyl ether prior to analysis to avoid adverse effects on the GC columns by DMF. The ethereal layer was dried over $CaCl_2$ prior to analysis.

The GC liquid phases used were those aforementioned. Samples of all effluent components were isolated and identified by comparison of IR spectra with those of authentic samples or those in the "Aldrich Library of Infrared Spectra".[8] A comparison was also made of all absorptions of the components of the reaction mixture. No extraneous absorptions were detected.

Acknowledgments. Support of this work by the National Science Foundation (Grants GY-7101 and GU-3431) and Eastern New Mexico University is gratefully acknowledged.

Registry No.—Nickel, 7440-02-0; sodium borohydride, 16940-66-2; palladium, 7440-05-3.

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Nucleophilic Cleavage Reactions of Cyclic and Acyclic α-Diazo-β-ketophosphoryl Compounds

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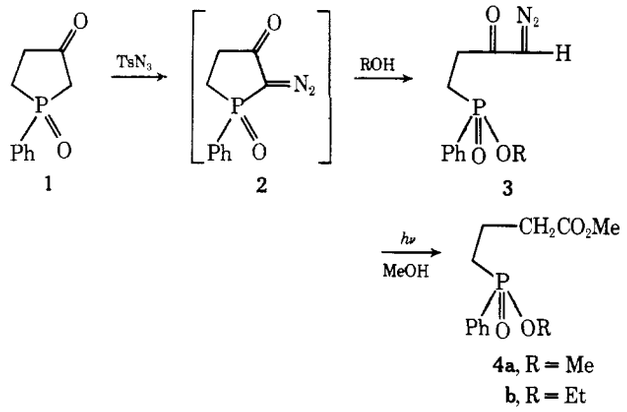
Acyl cleavage reactions of diazocarbonyl compounds have only recently achieved a measure of preparative importance, although they have long been known. The reaction has been shown to be useful for the preparation of α-diazocarboxylates,[1] α-diazo ketones,[2] and α-diazo sulfones[3] from the corresponding acyl derivatives which are readily available via the diazo transfer reaction. In the course of our studies on cyclic phosphorus compounds, we became interested in the five-membered cyclic diazoketophosphoryl compound (**2**) which might be converted to the phosphetane system via photochemical ring contraction. Thus, we attempted to prepare 2-diazo-3-phospholanone oxide (**2**) and found that the ring system in **2** was unstable, leading to ring cleavage exclusively at the P–C bond when treated with an alcohol containing amine.

For comparative purposes, we also examined the reaction of acyclic diazoketophosphoryl compounds under similar conditions.

Treatment of a methanol solution of 1-phenyl-3-phospholanone oxide (1) containing a slight excess of triethylamine



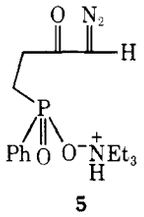
1 2 3

4a, R = Me
b, R = Et

with tosyl azide at 0 °C gave a yellow solution. After standing overnight at room temperature, the mixture was freed of solvent. Column chromatography on neutral alumina with chloroform gave acyclic diazo compound (**3a**) and tosyl amide in 81 and 78% yields, respectively, indicating that ring opening at P–C occurred during the reaction. The identity of **3** was confirmed on the basis of spectral data. The infrared spectrum of **3a** showed a prominent diazo absorption at 2140 cm^{-1} and a carbonyl at 1640 cm^{-1}, characteristic of simple acyclic diazo ketone.[2b] The NMR spectrum of **3a** showed a sharp 3 H doublet at δ 3.59 ppm with J_{PH} = 11.2 Hz, characteristic of $POCH_3$, and singlet at δ 5.27 ppm due to the $COCH{=}N_2$ proton. Further evidence concerning the acyclic structure of **3a** was derived from its efficient conversion to methyl carboxylate (**4**) via a photochemical Wolff rearrangement in methanol.

Ethyl phosphinate (**3b**) was similarly obtained by similar treatment in ethanol. In no case did we detect any product derived from an acyl cleavage reaction.

In an attempt to isolate cyclic diazo compound (**2**), the reaction was carried out in aprotic solvents, e.g., dry acetonitrile, acetone, or chloroform. However, in all cases the only neutral product isolable by column chromatography was tosyl amide (80–85% yield); no trace of cyclic diazo compound (**2**) could be isolated. Yellow material at the top of the column was extractable only with alkaline solution, e.g., a methanol solution of triethylamine. The extract was allowed to evaporate to dryness, leaving a yellow, viscous oil, which was tentatively assigned as the triethylamine salt of diazoketophosphinic acid (**5**) from its spectral data.



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When the reaction was carried out in acetonitrile followed by addition of excess methanol after all tosyl azide had reacted, a 23% yield of **3** was obtained by column chromatography, indicating the transient presence of **2** in solution.

In connection with the observed exclusive phosphoryl cleavage of cyclic system **2** in alcohol with weak base, it is of special interest to examine the behavior of acyclic α-diazo-β-ketophosphonates under similar conditions. Regitz et al.[4] have obtained benzoyldiazomethane as a by-product in the diazo transfer reaction of benzoylphosphonylmethane in the presence of phenyllithium, presumably arising from a phosphoryl cleavage of diazoketophosphonate during aqueous workup. Therefore, **6a** was stirred in methanol containing triethylamine overnight at room temperature. Contrary to the results of Regitz, we found that methyl benzoate and diazomethylphosphonate (**7**) derived from an acyl cleavage were formed in 80 and 78% yields, respectively. Neither phosphate (**8a**) nor benzoyldiazomethane could be isolated even though careful GC analysis of the crude reaction mixtures showed the presence of a trace amount (<1%) of phosphate. The present reaction affords a more convenient method for the preparation of the parent diazophosphonate compared to the reported[5] procedure in which direct diazotization of the corresponding amine was used because of the nonexistence and presumed instability of the required carbonyl precursor [$HCOP(O)(OR)_2 \rightarrow HP(O)(OR)_2 + CO$].

The reaction using acetyl derivative (**6b**) was much more convenient since the cleavage fragment (methyl acetate) was easily removable by evaporation under reduced pressure, leaving diazo compound (**7**) in a relatively uncontaminated state.

In order to clarify whether the observed difference in the cleavage positions between **2** and **6** is due to the phosphine oxide vs. phosphonyl functionality or to the cyclic vs. acyclic system, we also treated α-diazobenzylphosphine oxide (**6c**) with methanol containing amine. Methyl benzoate and diazomethylphosphine oxide (**7c**) were isolated again as main products in 88 and 86% yields, respectively, along with small amounts of phosphinate (**8c**) and benzoyldiazomethane, suggesting an obvious preference for acyl cleavage in the acyclic system. The noted increase in the yield of the phosphoryl cleavage is consistent with the fact that phosphinate is hydrolyzed by hydroxide more easily than phosphate.[6]

Experimental Section

General. Infrared spectra were determined on a JASCO IR-G recording spectrometer. Proton magnetic resonance spectra were determined on a JEOL JNM-MH-100 NMR spectrometer: chemical shifts are reported in units of δ (parts per million) downfield from Me_4Si. Mass spectra were obtained on a Shimadzu GC-MS 1000 spectrometer. GC analysis was performed on a Yanagimoto instrument Model G-80 using a column consisting of 10% SE-30 on Diasolid L (5.0 mm × 2.0 m). Woelm neutral alumina (activity III) was always used for column chromatography.

Starting Materials. Tosyl azide,[1] diazoketophosphonate,[4] and diazoketophosphine oxide[7] were prepared by literature procedures.

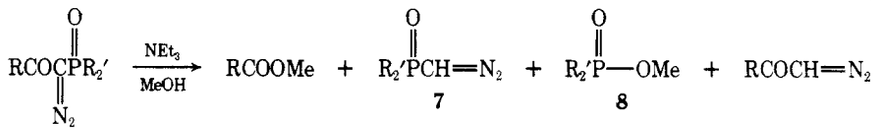
Phenylphospholanone oxide (1) was prepared from chloroprene and phenylphosphonous dichloride according to the literature[8] procedure for *P*-methyl derivative and recrystallized from dry benzene: mp 159–161 °C; IR ($CHCl_3$) ν 3380 (OH), 1738 (C=O), 1590 (C=C), and 1180 cm^{-1} (P=O); NMR ($CDCl_3$) δ 1.86–3.24 (m, $-CH_2-$), 4.89 (d, J = 18.8 Hz, C=CH of enol form), and 7.18–7.80 (m, C_6H_5).

Anal. Calcd for $C_{10}H_{11}O_2P$: C, 61.86; H, 5.71. Found: C, 62.03; H, 5.74.

Methyl Phenyl-4-diazo-3-ketobutylphosphinate (3a). To a cooled solution of 97 mg (0.5 mmol) of 1-phenylphospholanone oxide (1) and 70 mg (0.68 mmol) of triethylamine in 1.0 ml of dry methanol was added 99 mg (0.5 mmol) of tosyl azide with vigorous stirring over 10–15 min at 0 °C. The addition causes the reaction mixture to warm and assume a yellow color. The mixture was allowed to stand overnight at room temperature, and then all volatile components were evaporated at 20 °C under reduced pressure on a rotary evaporator. The resulting residue was chromatographed over neutral alumina using chloroform as the eluent.

The first fraction obtained, yellowish liquid (103 mg, 81%), was identified as phosphinate (**3**): IR ($CHCl_3$) ν 2140 ($C{=}N_2$), 1640 (C=O), 1195 (P=O), and 1040 cm^{-1} (POC); NMR ($CDCl_3$) 2.13–2.73 (m, 4 H, $-CH_2-$), 3.59 (d, 3 H, J = 11.2 Hz, POMe), 5.27 (s, 1 H, $CH{=}N_2$), and 7.37–7.91 (m, 5 H, C_6H_5); mass spectrum m/e 224 ($M^+ - 28$), 196, 168.

The second fraction, obtained as white crystals (130 mg, 76%), was



6a, R = Ph; R′ = OEt	80%	78%	<1%	
b, R = Me; R′ = OEt		90%		
c, R = R′ = Ph	88%	86%	12%	10%

identified as tosyl amide by comparison of its IR and NMR spectra with those of an authentic sample.

Ethyl Phosphinate (3b). Using ethanol as solvent in the above procedure gave a 78% yield of **3b:** IR ($CHCl_3$) ν 2140 (C=N_2), 1640 (C=O), 1193 (P=O), and 1035 cm^{-1} (POC); NMR ($CDCl_3$) δ 1.28 (t, J = 7.0 Hz, 3 H, CH_2CH_3), 2.16–2.82 (m, 4 H, $-CH_2-$), 3.86 (d, J_{PH} = 7.0 Hz, of q, J_{HH} = 7.0 Hz, 2 H, $POCH_2CH_3$), 5.24 (s, 1 H, CH=N_2), and 7.26–7.80 (m. 5 H, C_6H_5); mass spectrum *m/e* 238 ($M^+ - 28$), 210, 182.

Attempt to Isolate 2-Diazo-3-phospholanone Oxide (2). To a solution of 194 mg (1.0 mmol) of phospholanone oxide (1) and 140 mg of triethylamine in 2.0 ml of dry acetonitrile was added 198 mg (1.0 mmol) of tosyl azide and the mixture was kept overnight at room temperature. TLC analysis of the reaction mixture showed that no tosyl azide was present at the end of this time.

To one-half of the solution was added 1.0 ml of dry methanol and the resulting solution was allowed to stir overnight. The solvent was removed under reduced pressure and the residue was chromatographed in the usual way. The foreband gave acyclic diazophosphinate (**3a**) (28 mg, 23%); further elution with chloroform afforded tosyl amide (66 mg, 77%).

The second half of the reaction mixture was evaporated under reduced pressure, followed by chromatography. Only tosyl amide (70 mg, 82%) was eluted from the column. The yellow material adsorbed on the alumina at the top of the column was extracted with 10% triethylamine in methanol and the extract was evaporated to dryness under vacuum to give **5** as a sticky yellow oil, which failed to crystallize upon standing: IR ($CHCl_3$) ν 2400, 2250 (N^+H), 2140 (C=N_2), 1640 (C=O), 1190 cm^{-1} (P=O); NMR ($CDCl_3$) δ 1.10 (t, J = 8 Hz, 9 H, CH_2CH_3), 1.75–2.68 (m, 4 H, $-CH_2-$), 2.95 (q, J = 8 Hz, 6 H, CH_2CH_3), 3.41 (s, 1 H, ^+NH), 5.33 (s, 1 H, CH=N_2), and 7.20–7.95 (m, 5 H, C_6H_5).

Photolysis of 3 in Methanol. A solution of 56 mg of **3a** in 1 ml of methanol was placed in a quartz tube and irradiated for 5 h at 12 °C with a 300-W medium-pressure mercury lamp. After removal of solvent under vacuum, the residue was chromatographed on alumina using chloroform to afford 26.7 mg (80%) of methyl carboxylate **4a** as a colorless liquid: ir ($CHCl_3$) ν 1730 (C=O), 1179 (P=O), and 1040 cm^{-1} (POC); NMR ($CDCl_3$) δ 1.65–2.57 (m, 6 H, $-CH_2-$), 3.63 (d, J = 11.3 Hz, 3 H, POMe), 3.65 (s, 3 H, COOMe), and 7.38–8.18 (m, 5 H, C_6H_5); mass spectrum *m/e* 256 (M^+), 225, 197.

Anal. Calcd for $C_{12}H_{17}O_4P$: C, 56.25; H, 6.69; P, 12.09. Found: C, 56.12; H, 6.70; P, 11.96.

Using **3b** in the above procedure gave **4b** in 63% yield: IR ($CHCl_3$) ν 1730 (C=O), 1190 (P=O), and 1036 cm^{-1} (POC); NMR ($CDCl_3$) δ 1.30 (t, J = 6.6 Hz, 3 H, $POCH_2CH_3$), 1.71–2.55 (m, 6 H, $-CH_2-$), 3.46 (s, 3 H, OMe), 4.02 (d, J_{PH} = 6.6 Hz, of q, J_{HH} = 6.6 Hz, 2 H, $POCH_2CH_3$), and 7.37–7.95 (m, 5 H, C_6H_5); mass spectrum *m/e* 270 (M^+), 239, 211.

Anal. Calcd for $C_{13}H_{19}O_4P$: C, 57.77; H, 7.09; P, 11.46. Found: C, 57.60; H, 7.13; P, 11.10.

Diethyl Diazomethylphosphonate (7). A. From Benzoyl Derivative (6a). To a solution of 84 mg (0.3 mmol) of diethyl α-diazophenacylphosphonate (**6a**) in 0.5 ml of dry methanol was added 33 mg (0.32 mmol) of triethylamine in 0.5 ml of methanol at room temperature. The solution was stirred vigorously overnight at the same temperature. GC analysis of the reaction mixture at the end of this time indicated the presence of methyl benzoate and a trace amount of methyl diethyl phosphate. Volatile components were removed from the resulting red solution under reduced pressure at 20 °C and the residue was chromatographed on alumina.

The first fraction was methyl benzoate (33 mg, 80%), identified by IR and NMR comparison with an authentic sample.

The second fraction was diazomethylphosphonate (**7a,** 42 mg, 78%), yellow liquid: IR ($CHCl_3$) ν 2142 (C=N_2), 1250 (P=O), and 1024 cm^{-1} (POC); NMR ($CDCl_3$) δ 1.37 (t, J = 7.2 Hz, 6 H, $POCH_2CH_3$), 3.68 (d, J = 10.8 Hz, 1 H, CH=N_2), and 4.08 (d, J_{PH} = 7.2 Hz, of q, J_{HH} = 7.2 Hz, 4 H, $POCH_2$).

B. From Acetyl Derivative (6b). To a solution of 137 mg (0.62 mmol) of **6b** in 1.0 ml of methanol was added 80 mg of triethylamine. After stirring overnight at room temperature, all volatile components were rigorously evaporated under reduced pressure at 30 °C to give yellow liquid (101 mg, 90%), which showed essentially identical NMR and IR spectra with those of **7** obtained above.

Diphenyldiazomethylphosphine Oxide (7c). Treatment of a suspension of 208 mg (0.6 mmol) of **6c** in 1.0 ml of methanol with 80 mg (0.8 mmol) of triethylamine as above resulted in a clear solution. Chromatography of the reaction mixture as usual manner gave the following products in their order of separation. Methyl benzoate (71.8 mg, 88%); benzoyldiazomethane [8.9 mg, 10%; IR ($CHCl_3$) ν 2125 (C=N_2) and 1612 cm^{-1} (C=O); NMR ($CDCl_3$) δ 5.92 (s, 1 H, CH=N_2) and 7.35–7.84 (m, 5 H, C_6H_5)]; **8c** [17.4 mg, 12%; NMR ($CDCl_3$) 3.67 (d, J_{PH} = 12.0 Hz, 3 H, POMe) and 7.28–7.92 (m, 5 H, C_6H_5)]; **7c** [124.5 mg, 86%; IR ($CHCl_3$) ν 2120 (C=N_2) and 1282 cm^{-1} (P=O); NMR ($CDCl_3$) 4.20 (d, J_{PH} = 12.1 Hz, 1 H, CH=N_2) and 7.34–7.81 (m, 5 H, C_6H_5)].

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Registry No.—**1,** 60705-77-3; **3a,** 60705-78-4; **3b,** 60705-79-5; **4a,** 60705-80-8; **4b,** 60705-81-9; **5,** 60705-83-1; **6a,** 19734-16-8; **6b,** 21047-57-4; **6c,** 17507-54-9; **7a,** 25411-73-8; **7c,** 5353-66-2; **8a,** 867-17-4; **8c,** 1706-90-7; PhCOOMe, 93-58-3; PhCOCH=N_2, 3282-32-4; tosyl azide, 941-55-9; tosyl amide, 70-55-3.

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A Simple, High Yield Method for the Nucleophilic Substitution of Halonitrobenzenes by Thiols

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Although the use of direct thioalkylation of halonitrobenzenes is often a convenient route to the corresponding thioanisoles,[1] the desired reaction can be almost completely precluded by reduction of the nitro group.[2] During the course of other work, we required thioanisole **2b** (R = CH_3) as an intermediate. In attempting to prepare this compound by the method of Hodgson and Handley,[1,2] we obtained **2b** (R = CH_3) in only 18% yield, the remainder consisting of the three possible azoxybenzenes **3b–d** (R = CH_3).[3]

It occurred to us that this problem might be readily overcome by forming the thiolate anion in the presence of both excess thiol[4] and aromatic substrate. This was readily carried out by the dropwise addition of methanolic KOH to **1b** in the