Experimental Section

Methyl 3-Arsabenzenecarboxylate and Methyl 2-Arsabenzenecarboxylate. A solution of 1.7 g (12 mmol) of arsabenzene and 2.3 g (27 mmol, 2.2 equiv) of methyl propiolate in 20 mL of mesitylene was heated at 120 °C for 15 h, after which all low-boiling materials were removed by vacuum distillation. Analysis of the residue by GLC ($^1/_4$ in. × 8 ft column, packed with 20% Carbowax 20-M on Chromosorb W at 185 °C) showed methyl 1-arsabicyclo[2.2.2]octa-2,5,7-triene-3- and -2-carboxylate present in the ratio of 63:37. The mixture of carboxylates was used without further purification.

A solution of the two carboxylates obtained above and 2.8 g (12 mmol) of 3,6-bis(2-pyridyl)tetrazine in 20 mL of methylene chloride was stirred for 16 h. GLC ($^1/_4$ in. × 5 ft column packed with 5% SE-30 on Chromosorb W at 150 °C) showed no unreacted starting materials. The suspension was then filtered, and the residue was washed with cold benzene. The solvent was then removed from the filtrate and the residual oil distilled under vacuum to give a light yellow oil: bp 67 °C (0.1 torr); yield 1.67 g (70% based on arsabenzene).

GLC analysis ($^1/_4$ in. × 5 ft column packed with 15% XF-1150 on Chromosorb W at 175 °C) of the oil showed the presence of methyl 3- and 2-arsabenzenecarboxylate in the ratio of 62:38. The two carboxylates can be separated by preparative GLC and were found to be identical with those obtained by the pyrolysis of the corresponding methyl arsabicyclo[2.2.2]octatrienecarboxylates.[11]

3-Arsabenzenecarboxylic Acid. To a solution of 102 mg (1.9 mmol) of sodium methoxide in 10 mL of 1:1 (v/v) water–methanol was added 119 mg (0.6 mmol) of methyl 3-arsabenzenecarboxylate in 200 μL of methanol. The mixture was heated at 70 °C for 15 h. It was then extracted once with methylene chloride, which was found to contain no starting material. The base was then neutralized with a solution of 409 mg (2.15 mmol) of *p*-toluenesulfonic acid monohydrate in 5 mL of water, and the product was extracted into methylene chloride (4 × 7 mL). Removal of solvent by distillation gave a white solid. The crude yield was 111 mg (100%). A 98-mg sample was recrystallized from 6 mL of water to give 70 mg (71%) of white needles: mp 86 °C; ^{1}H NMR ($CDCl_3$) δ 8.07 (1 H, t, J = 9 Hz), 8.43 (1 H, d, J = 9 Hz), 10.03 (1 H, d, J = 9 Hz), 10.63 (1 H, s), 11.67 (1 H, br s); mass spectrum, m/e 184 (M^+, $C_6H_5AsO_2$, base peak). Anal. Calcd for $C_6H_5AsO_2$: C, 39.16; H, 2.74. Found: C, 39.21; H, 2.84.

2-Arsabenzenecarboxylic Acid. An analogous procedure was followed by using the following amounts of materials: 103 mg (1.9 mmol) of sodium methoxide, 127 mg (0.64 mmol) of methyl 2-arsabenzenecarboxylate, and 418 mg (2.20 mmol) of *p*-toluenesulfonic acid monohydrate. The crude yield was 110 mg (93%). A 93-mg sample was recrystallized from 6 mL of water to give 71 mg (76%) of yellow needles: mp 86 °C; ^{1}H NMR ($CDCl_3$) δ 7.70 (1 H, t, J = 8 Hz), 8.03 (1 H, t, J = 8 Hz), 8.70 (1 H, d, J = 8 Hz), 9.87 (1 H, d, J = 8 Hz), 11.85 (1 H, bs); mass spectrum, m/e 184 (M^+, $C_6H_5AsO_2$, base peak). Anal. Calcd for $C_6H_5AsO_2$: C, 39.16; H, 2.74. Found: C, 39.00; H, 2.80.

Determination of Dissociation Constants. The ionization constants of benzoic acid, 2-arsabenzenecarboxylic acid, and 3-arsabenzenecarboxylic acid at 20.0 ± 0.1 °C were determined by potentiometric titration under nitrogen, with a Radiometer titrator TTT2 and a Radiometer ABU 12 autoburet. The glass electrode was standardized before and after each determination. The method of Albert and Serjeant was used to determine the pK_a values.[17]

Acknowledgment. Support of our work by the National Institutes of Health (Grant No. RO1-GM-20992) is gratefully acknowledged.

Registry No. Arsabenzene, 289-31-6; methyl propiolate, 922-67-8; methyl 1-arsabicyclo[2.2.2]octa-2,5,7-triene-3-carboxylate, 63787-93-9; methyl 1-arsabicyclo[2.2.2]octa-2,5,7-triene-2-carboxylate, 63787-94-0; methyl 3-arsabenzenecarboxylate, 63787-90-6; methyl 2-arsabenzenecarboxylate, 63787-91-7; 3-arsabenzenecarboxylic acid, 73178-35-5; 2-arsabenzenecarboxylic acid, 73178-36-6; benzoic acid, 65-85-0.

(17) Albert, A.; Serjeant, E. P. "Ionization Constants of Acids and Bases"; Methuen and Co., Ltd.: London, 1962.

Syntheses with α-Heterosubstituted Phosphonate Carbanions. 10.[1a] Autoxidation of the Anion

Hans Zimmer,*[1b] Rusty E. Koenigkramer,[1c] R. L. Cepulis,[1d] and D. M. Nene

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

Received December 3, 1979

The autoxidation of alkylidenetriphenylphosphoranes (ylides) has been found to be a valuable method for the preparation of symmetrical olefins[2,3] including cyclic ones.[4,5] A similar method for the preparation of symmetrical olefins by autoxidation of the carbanion of benzyldiphenylphosphine oxide was reported by Horner and co-workers.[6] Ketones were obtained by the same author by autoxidation of (1-phenylalkyl)diphenylphosphine oxides.

In this report the autoxidation of the anions derived of diphenyl [aryl[(4-nitrophenyl)amino]methyl]phosphonates will be described which leads to the formation of the corresponding aroyl anilides. The phosphonates which are starting materials for this reaction are easily obtained in a one-pot reaction from diphenyl phosphite, an aniline, and an aromatic aldehyde[7,8] (Table I). They are transformed into the corresponding α-heterosubstituted phosphonate carbanions smoothly by using potassium *tert*-butoxide in dimethyl sulfoxide as base. For the autoxidation, the carbanions were placed under 50 psi of oxygen and shaken for 12 h. In every case the corresponding anilide (Table II) was isolated in a fair to good yield.

Discussion

The overall reaction sequence for the autoxidation of ylides was formulated by Bestmann[3] as in Scheme I. The ylide was cleaved by oxygen initially into one molecule of triphenylphosphine oxide and a molecule of aldehyde. The latter then reacts with an unoxidized ylide in a typical Wittig reaction to give the final products, the symmetrical olefin and a second molecule of triphenylphosphine oxide.

The mechanism of the autoxidation of the diphenyl [aryl[(4-nitrophenyl)amino]methyl]phosphonates of this study has not been investigated. Neither we nor the earlier investigators[3,5] have any evidence to decide upon the detailed mechanism of the oxygen carbanion interaction. Two modes of reaction seem to be the most reasonable: (a) the oxygen and the carbanionic species react in a concerted manner to form a 1,2-dioxaphosphetane as an intermediate which fragments into products, or (b) a peroxide intermediate forms first which collapses via the four-membered intermediate into products (Scheme II). In the light of recent findings it seems more probable to assume that the oxygen in the highly basic solution reacts

(1) (a) Paper 9: Rusty E. Koenigkramer and Hans Zimmer, *Tetrahedron Lett.*, 1017 (1980); (b) presented in part at the ACS/CSJ Chemical Congress, Hawaii, Apr 1979, Abstract No. ORGN 508; (c) projected Ph.D. Thesis, University of Cincinnati, June 1980; (d) M.S. Thesis, University of Cincinnati, 1977.

(2) H. J. Bestmann, *Angew. Chem.*, **72**, 34 (1960).

(3) H. J. Bestmann and O. Kratzer, *Chem. Ber.*, **96**, 1899 (1963).

(4) H. J. Bestmann, H. Haberlein, and O. Kratzer, *Angew. Chem., Int. Ed. Engl.*, **3**, 226 (1964).

(5) H. J. Bestmann, *Angew. Chem., Int. Ed. Engl.*, **4**, 830 (1965).

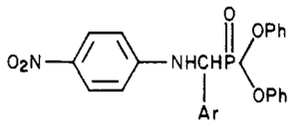
(6) L. Horner, H. Hoffmann, G. Klahre, V. G. Toscano, and H. Ertel, *Chem. Ber.*, **94**, 1987 (1961).

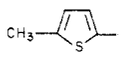
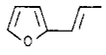
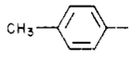
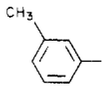
(7) E. K. Fields, *J. Am. Chem. Soc.*, **74**, 1528 (1952).

(8) Hans Zimmer and D. M. Nene, *J. Heterocycl. Chem.*, **15**, 1237 (1978), and additional references therein.

0022-3263/80/1945-2018$01.00/0

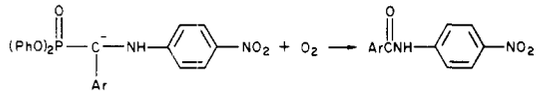
Table I

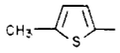
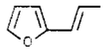
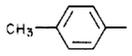
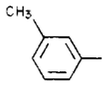


Ar	mol formula	mp, °C	yield, %	recrystallization solvent[a]
	$C_{23}H_{19}N_2O_5PS$	150-152	75	ethyl acetate
	$C_{24}H_{21}N_2O_5PS$	126-128	77	2-propanol
	$C_{24}H_{21}N_2O_5PS$	164-166	78	ethyl acetate
	$C_{25}H_{21}N_2O_6P$	170-172	84	ethyl acetate
	$C_{26}H_{23}N_2O_5P$	190-191.5	75	2-propanol
	$C_{26}H_{23}N_2O_5P$	158-159	78	ethyl acetate
Fe[b]	$C_{29}H_{25}FeN_2O_5P$	213 dec	86	THF/Et_2O

[a] All compounds gave C, H, and N analyses within 0.4% of the calculated values. [b] Fe = ferrocenyl group.

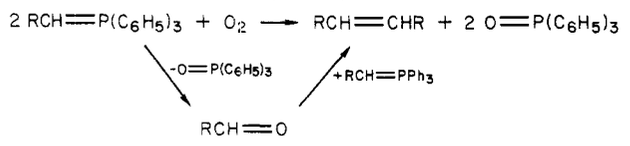
Table II



Ar	mol formula	mp, °C (95% EtOH)	yield,[g] %
	$C_{11}H_8N_2O_3S$	222-224[a]	47
	$C_{12}H_{10}N_2O_3S$	171-172	40
	$C_{12}H_{10}N_2O_3S$	205-207	60
	$C_{13}H_{10}N_2O_4$	245-247[b]	76
	$C_{14}H_{12}N_2O_3$	204-206[c,d]	51
	$C_{14}H_{12}N_2O_3$	142-144[d]	55
Fe[e]	$C_{12}H_{14}FeN_2O_3$	266-268 dec[f]	15

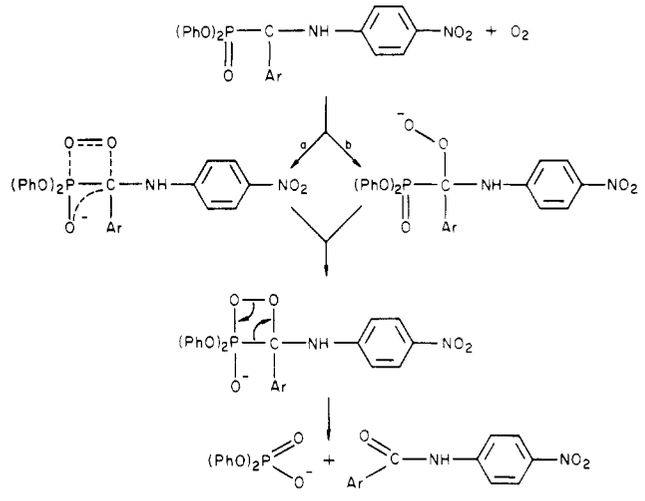
[a] Melting point 210 °C: G. Alberghina, A. Arcoria, S. Fisichella, and G. Scarlata, *Spectrochim. Acta, Part A*, 28, 2063 (1972). [b] See ref 13; mp 236-237 °C. [c] See ref 14; mp 201-203 °C. [d] $CHCl_3$. [e] Fe = ferrocenyl group. [f] Ethyl acetate. [g] All compounds gave C, H, and N analysis within 0.4% of the calculated values.

Scheme I

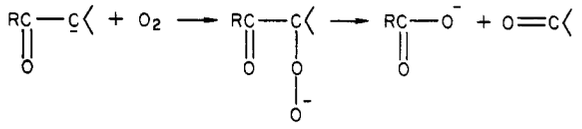


according to pathway b with the anionic carbon first before forming a four-membered intermediate. Such a peroxide was already discussed by Horner,[6] not excluded by Bestmann,[3] and it was later actually established in the aut-

Scheme II



Scheme III



oxidation of ketones in basic solution[9,10] that the reaction is somewhat similar to the one in Scheme III.

Though preparatively not as valuable as the autoxidation of triphenylmethylenephosphoranes[2-5] and of certain phosphine oxides[6] the method described here might very well be the method of choice to transform aromatic aldehydes in a two-step synthesis into the corresponding acid anilides, especially 4-nitroanilides (Table II). There are several known methods for the preparation of anilides. Among these are the Bodroux reaction,[11] in which an ester is treated with an aminomagnesium halide, and the Schotten-Baumann reaction,[12] in which an acid halide is

(9) H. R. Gersmann and A. F. Bickel, *J. Chem. Soc. B*, 2230 (1971).
(10) R. C. P. Cubbon and C. Hewlett, *J. Chem. Soc. C*, 2978 (1968).
(11) H. L. Bassett and C. R. Thomas, *J. Chem. Soc.*, 1188 (1954), and references therein.

reacted with an aniline. Other methods include the reaction of an acid anhydride with an aniline under pressure[13] and the reaction of a carboxylic acid with an aniline under dehydrating conditions.[14] In all of these methods, the formation of 4-nitroanilides is one of the most difficult ones because of the low basicity of 4-nitroaniline or the interference of the nitro group with the aminomagnesium halide reagent,[11] respectively. The yields reported here for the 4-nitroanilides range from fair to good. The anilides were identified by their elemental analysis, by UV, IR, NMR spectra,[1a] and, when available, by comparison with authentic materials. The reported yields are based on one run only. In attempts to optimize the yield of this autoxidation reaction by using 18-crown-6 ether or hexamethylphosphoric triamide (HMPT),[15] no significant improvement was obtained.

Experimental Section

All melting points are uncorrected. The elemental analyses were performed by Integral Microanalytical Laboratories.

The general procedure for the preparation of anilides is as follows. In a Parr pressure bottle, the phosphonate (0.005 mol) was dissolved in 10 mL/g of Me_2SO. To this solution, potassium *tert*-butoxide (0.0055 mol) was added. Quickly, the bottle was stoppered and placed on a Parr hydrogenation low-pressure apparatus and filled with oxygen until a pressure of 50 psi was reached. After 12 h, the now dark solution was diluted with 250 mL of H_2O and extracted twice with ethyl ether. The combined ether extracts were successively washed with water and brine and then dried over anhydrous sodium sulfate. Evaporation of the ether under vacuum left a clean solid residue which was recrystallized from a suitable solvent.

Acknowledgment. This investigation was partially supported by Grant CA-16666, awarded by the National Cancer Institute, DHEW.

Registry No. 1, 73230-90-7; 2, 73230-91-8; 3, 73230-92-9; 4, 73230-93-0; 5, 73230-94-1; 6, 73230-95-2; 7, 73246-60-3; 8, 39880-88-1; 9, 73230-96-3; 10, 73230-97-4; 11, 15341-97-6; 12, 33667-88-8; 13, 73230-98-5; 14, 73261-73-1.

(12) V. Gold, J. Hilton, and E. G. Jefferson, *J. Chem. Soc.*, 2756 (1954), and references therein.
(13) L. F. Golovyashkina, *Uzb. Khim. Zh.*, 11, 24 (1967); *Chem. Abstr.*, 64136 (1967).
(14) H. R. Snyder and C. T. Elston, *J. Am. Chem. Soc.*, **76**, 3039 (1954). Using *p*-nitroaniline in their method, these authors obtained a yield of 0% of the desired *p*-nitroanilide.
(15) H. J. Bestmann and W. Stransky, *Synthesis*, 798 (1974).

Studies on Ketene and Its Derivatives. 98.[1] 1,1-Dichloro-5-oxo-4-oxaspiro[2.3]hexane. Synthesis and Reactions

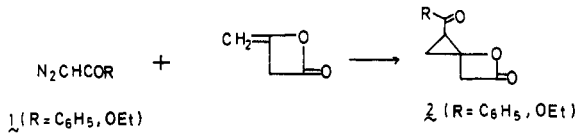
Tetsuzo Kato,* Takuo Chiba, Renzo Sato, and Toshimitsu Yashima

Pharmaceutical Instutite, Tohoku University, Aobayama, Sendai 980, Japan

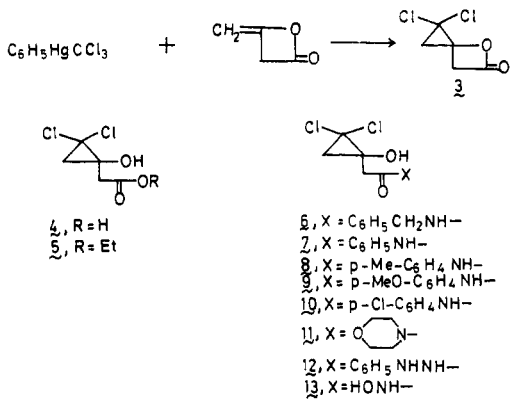
Received July 13, 1979

Previously, we reported that α-diazo ketones and esters, such as diazoacetophenone (1, R = Ph) and ethyl diazoacetate (1, R = OEt), react with diketone to give the spiro compounds 1-benzoyl- (and 1-ethoxycarbonyl-) 5-oxo-4-oxaspiro[2.3]hexane (2, R = Ph and OEt)[2,3] (see Scheme I). The reaction involves [1 + 2] cycloaddition of a carbene generated from the diazo compound to the exo methylene of diketene. In the present paper, we describe that the reaction of diketene with phenyl(trichloromethyl)mercury, which can be regarded as a carbene precursor, proceeds in a similar fashion to give a spiro compound. Furthermore, we have investigated some reactions of the product to give cyclopropaneacetic acid derivatives in which the cyclopropane ring remains intact. Since the reactions of the cyclopropanespirolactones of type 2 under the same conditions gave ring-opened products, it is of interest that dichlorocyclopropanespirolactone does not suffer opening of the three-membered ring. These results are another subject of the present paper.

Scheme I



Scheme II



When a solution of phenyl(trichloromethyl)mercury and diketene in dry benzene was refluxed, the spiro compound 1,1-dichloro-5-oxo-4-oxaspiro[2.3]hexane (3) was obtained in 25% yield (see Scheme II). When dry toluene was used as a solvent instead of benzene, the reaction proceeded more smoothly to give 3 in 72% yield.

Structure assignment of the products was made on the basis of elemental analyses, spectral data, and chemical behavior. Specifically, the IR spectrum of 3 showed the presence of the β-lactone carbonyl at 1865 cm^{-1}, and the NMR spectrum indicated two AB quartet signals assignable to the methylene groups of the cyclopropane and β-lactone rings at δ 1.84–2.27 and 3.47–4.10, respectively.

Hydrolysis of spiro product 3 with 10% hydrochloric acid afforded 2,2-dichloro-1-hydroxycyclopropaneacetic acid (4) in 60% yield. In its IR spectrum the β-lactone carbonyl absorption had disappeared and hydroxyl and carboxylic acid absorptions were observed at 3600–2400, 3530, and 1715 cm^{-1}. The NMR spectrum showed two singlet signals due to the methylene groups of the cyclopropane and acetic acid moieties at δ 1.69 and 2.97, respectively.

Treatment of 3 with dry hydrogen chloride in absolute ethanol gave ethyl 2,2-dichloro-1-hydroxycyclopropaneacetate (5) as a colorless oil in 81% yield. As detailed in the Experimental Section, the IR and NMR spectra were consistent with ester structure 5.

Treatment of 3 with an alkali such as sodium bicarbonate in water or sodium ethoxide in ethanol resulted

(1) No. 97: T. Kato, T. Chiba, and S. Tsuchiya, *Chem. Pharm. Bull.*, **28**, 327 (1980).
(2) T. Kato, N. Katagiri, and R. Sato, *J. Chem. Soc., Perkin Trans. 1*, 525 (1979).
(3) T. Kato and N. Katagiri, *Chem. Pharm. Bull.*, **21**, 729 (1973).

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