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Thermally Labile Ketenimines from Triphenylphosphinalkylimines

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A recent study in our laboratory of a 1,3-nitrogen to carbon rearrangement (ketenimine → nitrile)[1] required routes to thermally labile and chiral ketenimines in which the asymmetric center was directly attached to the nitrogen. We wish to report our experience with the synthetic sequence shown in Scheme I. The key step is the reaction of

Scheme I

$$Ph_3P \xrightarrow[\text{benzene}]{1\text{ equiv } Br_2} \underset{2}{Ph_3PBr_2} \xrightarrow[1\text{ equiv } (C_2H_5)_3N,\ \text{benzene}]{1\text{ equiv } RR'R''CNH_2} [Ph_3PNHCRR'R'']^+Br^- \xrightarrow[\text{ether}]{\text{excess KOH}} \underset{4}{Ph_3P{=}NCRR'R''} \xrightarrow[\text{Ether}]{Ph_2C{=}C{=}O} Ph_2C{=}C{=}NCRR'R'' + Ph_3PO$$

(3) (4) (5)

diphenylketene with a triphenylphosphinalkylimine, first reported many years ago by Staudinger and Hauser.[2] We believe our present procedures offer some advantages over those previously described. Further, we demonstrate that optically active ketenimines can be prepared by this route with no measurable racemization at the asymmetric center directly attached to the nitrogen.

Nearly stoichiometric yields of the phosphonium bromides (**3**) were obtained by the addition of a primary amine and 1 equiv of triethylamine[3] to the *in situ* prepared triphenylphosphine dibromide (**2**). Deprotonation to the phosphinalkylimine (**4**) was readily accomplished by simply stirring **3** over excess potassium hydroxide in anhydrous ether for 20–40 hr. Previous workers used sodamide.[3] It is our experience that excellent yields are obtained by our procedure.

Slow addition of an ether solution of **4** at room temperature to an ether solution of diphenylketene under nitrogen gives diphenyl-*N*-(substituted)ketenimines in good to excellent yields. It is important to note that thermally labile ketenimines, which cannot be prepared by the more vigorous dehydration and dehydrohalogenation procedures[4] are easily prepared by Scheme I. Some difficulties encountered tered in separating the last traces of triphenylphosphine oxide from the ketenimine were overcome by chromatographing the product mixture over basic alumina.

By this reaction sequence, we have successfully prepared the diphenylketenimines having N-substituents of *tert*-butyl (**6**), benzyl (**7**), and 1-phenylethyl (**8**). The diphenyl-*N*-(diphenylmethyl)ketenimine (**9**) apparently also is formed *via* Scheme I, but is too labile toward rearrangement[1] at room temperature for isolation since 2,2,3,3-tetraphenylpropionitrile is recovered.

A synthetic sequence starting with (*S*)-(−)-1-phenylethylamine ($\alpha^{25}D$ −37.0°, neat) *via* (*S*)-(−)-triphenylphosphin-*N*-(1-phenylethyl)imine ($[\alpha]^{25}D$ −62.4°, *c* = 14.4, CCl_4) yielded (*S*)-(−)-diphenyl-*N*-(1-phenylethyl)ketenimine ($[\alpha]^{25}D$ 35.3°, *c* = 5.21, CCl_4). This synthetic sequence proceeds with complete retention of configuration since mild hydrolysis[5] of (*S*)-(−)-**8** gives a 95% yield of (*S*)-(−)-diphenyl-*N*-(1-phenylethyl)acetamide showing the same specific rotation as amide directly prepared from starting (*S*)-(−)-1-phenylethylamine and diphenylacetyl chloride ($[\alpha]^{25}D$ −39.6°, *c* = 1.2, $CHCl_3$).

The scope of Scheme I is limited by (i) the thermal lability of the resulting ketenimines and (ii) the availability of reasonably stable ketenes. As a guide for point (i), we observed that the thermal thresholds for reaction of the diphenylketenimines in Table II are **6**, ~125°; **7**, ~70°; **8**, 50°; **9** ≳ 25°. With regard to (ii), it should be possible to extend this synthesis to ketenimines derived from other ketenes if the self-reactions of the latter do not interfere.

Table I
Properties of the Alkylaminotriphenylphosphonium Bromides and Triphenylphosphinalkylimines

			$[Ph_3PNHCRR'R'']^+Br^-$ [a]			$Ph_3P{=}NCRR'R''$ [b]		
R	R′	R″	Mp, °C	Registry no.	Nmr (CD_3Cl, δ)	Mp, °C	Registry no.	Nmr (CCl_4, δ)
Ph	H	H	195–197	52826-42-3	4.33 (2 H) q, 7.2–8.1 (20 H) m, 2.03 (1 H) s	137–138	52826-45-6	4.43 (2 H) d,[c] 7.0–8.0 (20 H) m
Ph	CH_3	H	156–157[d] 116–117[e]	52826-43-4 52918-35-1	1.87 (3 H) q, 4.13 (1 H) m, 2.17 (1 H) s, 7.1–8.1 (20 H) m	67–68[d] oil[e]	52826-46-7 52882-00-5	1.43 (3 H) q,[f] 4.37 (1 H) m,[c] 7.0–8.0 (20 H) m
Ph	Ph	H	267–269	52826-44-5	2.10 (1 H) s, 5.07 (1 H) q, 7.1–8.1 (25 H) m	129–131	52826-47-8	5.33 (1 H) d,[c] 7.0–8.0 (25 H) m
CH_3	CH_3	CH_3	165–167	799-51-9	1.33 (9 H) s, 7.2–8.2 (15 H) m, 2.37 (1 H) s	146–147	13989-64-5	1.17 (9 H) d,[f] 7.0–8.0 (15 H) m

[a] All isolated yields are in excess of 95%. [b] All isolated yields are in excess of 75%. [c] *J* (P = N–CH–) ~20 Hz. [d] Racemic modification. [e] *S*-(−) compound. [f] *J* (P = N–C–CH_3) ~1 Hz.

Table II
Important Data on the Diphenyl-*N*-(substituted)ketenimines

Ketenimines	Isolated Yield,[a] %	Nmr (CCl_4, δ)	Ir (cm^{-1})
6[b]	75–80	1.40 (9 H) s, 7.1–7.4 (10 H) m	2020
7[c]	65–70	4.73 (2 H) s, 7.0–7.4 (15 H) m	2020
8[d]	80–85	1.65 (3 H) d, 4.88 (1 H) q, 7.0–7.4 (15 H) m	2020

[a] After chromatography on alumina. [b] See ref 6 for combustion data. [c] Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94. Found: C, 88.94; H, 6.14; N, 4.90. [d] Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.74; H, 6.52; N, 4.65.

Experimental Section[7]

Alkylaminotriphenylphosphonium Bromides. Into a 300-ml three-necked flask equipped with a pressure-equalized addition funnel, a reflux condenser with a drying tube and an efficient electric stirrer was added 100 ml of benzene (reagent) and 0.1 mol of triphenylphosphine. The solution was cooled in an ice bath and 0.1 mol of bromine was added dropwise to the stirred solution over 0.5 hr. The mixture was stirred for an additional 0.5 hr (bromine color discharged), and a mixture of 0.1 mol of triethylamine and 0.1 mol of primary amine was added dropwise at ice bath temperature over 0.5 hr. The mixture was stirred for 1 hr at ice bath temperature, and the resulting precipitate was collected, washed with ether, and then water. The solid was dissolved in 50 ml of chloroform and crystallized by addition of 500 ml of ethyl acetate. Isolated yields were in excess of 95% in all cases.

Triphenylphosphinalkylimines. Into a 500-ml flask equipped with a reflux condenser fitted at the top with a nitrogen inlet tube, and arranged for magnetic stirring, was placed 20 mmol of the above prepared alkylaminophosphonium bromide, 50 mmol of potassium hydroxide pellets, and 250 ml of anhydrous ether. The mixture was stirred under nitrogen for 20–40 hr at room temperature. The mixture was then filtered and the ether removed *in vacuo*. The resulting solid was crystallized from cyclohexane. The isolated yields of the triphenylphosphinalkylimines were in excess of 75% in all cases.

Diphenyl-*N*-(substituted)ketenimines. Into a 500-ml three-necked flask equipped with a pressure-equalized dropping funnel fitted at the top with a nitrogen inlet tube and an efficient electric stirrer was placed 7 mmol of the above prepared triphenylphosphinalkylimine in 200 ml of anhydrous ether. Diphenylketene[8] dissolved in 30 ml of anhydrous ether was added dropwise to the stirred solution over 0.5 hr at room temperature. The mixture was stirred an additional 1 hr and the ether solution was washed three times with ice–water, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The resulting residue was chromatographed on basic alumina (Woelm) which had been dried at 125° for 2 hr. The ketenimine was recovered in an early fraction by eluting with ether–petroleum ether (4:1). Ketenimines **6**, **7**, and **8** were prepared in this way.

In the case of the preparation of diphenyl-*N*-(diphenylmethyl)ketenimine (**9**), the characteristic ketenimine band at 2020 cm^{-1} was noted in the ir of the crude reaction mixture. However, after concentration of the ether solution, the 2020-cm^{-1} band was gone. Chromatography yielded a material identified as 2,2,3,3-tetraphenylpropionitrile by comparison with a sample independently prepared by a phase transfer reaction.[9]

(*S*)-(−)-Diphenyl-*N*-(1-phenylethyl)ketenimine. (*S*)-(−)-**8** was prepared by the above procedures starting from (*S*)-(−)-1-phenylethylamine (Norse Chemical Co., Santa Barbara, Calif.). The optical purity of (*S*)-(−)-**8** was demonstrated as follows. (*S*)-(−)-**8** was hydrolyzed to the corresponding amide by a slight modification of a procedure described by Stevens and Singhal.[5] To a solution of 100 mg of (*S*)-(−)-**8** in 5 ml of acetone was added 0.5 ml of 4 *N* hydrochloric acid. The mixture was allowed to stand at room temperature for 2 hr. The solution was then cooled to 5° and water was added slowly until no further white precipitate formed. The mixture was placed in a refrigerator (5°) overnight and then filtered. The solid was collected, dried, and recrystallized from cyclohexane–hexane to give a 95% yield of amide, mp 116.0–116.5°, $[\alpha]^{25}D$ −39.6° (c = 1.2, $CHCl_3$). Amide showing the same properties and specific rotation was prepared by conventional procedures from (*S*)-(−)-1-phenylethylamine and diphenylacetyl chloride.

Registry No.—**6**, 26149-14-4; **7**, 52826-48-9; (*S*)-(−)-**8**, 52826-49-0; (*S*)-(−)-**8** amide derivative, 52826-50-3; **9**, 52826-51-4; benzylamine, 100-46-9; (±)-1-phenylethylamine, 618-36-0; (*S*)-(−)-1-phenylethylamine, 2627-86-3; diphenylmethylamine, 91-00-9; *tert*-butylamine, 75-64-9; triphenylphosphine, 603-35-0; bromine, 7726-95-6; diphenylketimine, 52826-52-5.

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A New Route to 2-Vinylaziridines and an Unusual Intramolecular Analog of the SN2′ Reaction Leading to Aziridine Ring Formation

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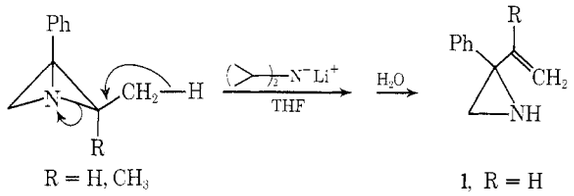
N-Unsubstituted 2-vinylaziridines have been obtained from butadiene[1a] and isoprene[1b] by modification of the Wenker aziridine synthesis, and as by-products in hydride reductions of isophorone oxime.[1c] N-Substituted 2-vinylaziridines have been synthesized *via* nitrene precursors and butadienes[2]

We report here a new method for the synthesis of certain N-unsubstituted 2-vinylaziridines by treatment of 2-methyl-substituted 1-azabicyclobutanes with strong base. Thus we have obtained 2-phenyl-2-vinylaziridine (**1**) and 2-phenyl-2-(2-propenyl)aziridine (**2**) from the reaction of *exo*-2-methyl-3-phenyl-1-azabicyclobutane[3] and 2,2-dimethyl-3-phenyl-1-azabicyclobutane,[3] respectively, with lithium diisopropylamide in THF.



The E2 or E1cB type of elimination which is occurring here involves the formation of an aziridinamide anion as a leaving group. It is noteworthy that such loss of a strongly basic amide anion is probably unknown to occur in elimination reactions.[4] The concommitant relief of ring strain is probably an important factor which allows the above reaction to proceed; in addition, coordination of Li^+ to the N of the azabicyclobutane may play an important role in giving the nitrogen more leaving-group character akin to that of the positively charged N in ammonium salts which can undergo Hofmann-type elimination.

2-Vinylaziridines are of interest as possible substrates for conversion to Δ^3-pyrrolines *via* thermal isomerization[5]