(b) To a solution of dienone **2** (100 mg) in anhydrous methanol, a catalytic amount of *p*-toluenesulfonic acid (10 mg) was added and the reaction mixture refluxed for 24 hr. Removal of solvent gave 105 mg of a material which was dissolved in ethyl acetate and washed with water. The ethyl acetate extract was dried and evaporated to give a semisolid (100 mg). Uv and nmr spectra of this material indicated the absence of **1**. The nmr spectrum instead indicated the presence of dienone **10**. Chromatography over silica gel gave pure **10** (25 mg, liquid) on elution with ether–benzene mixture (1:4). Further eluting the column with ethyl acetate gave the starting material, dienone **4**.

For combustion analysis the solid acetyl derivative of **10** was prepared. The acetyl derivative was crystallized from hexane to give colorless needles: mp 140°; uv max (MeOH) 258 mμ (ε 8420).

Anal. Calcd for $C_{11}H_{10}O_5Br_2$: C, 34.55; H, 2.61; Br, 41.88. Found: C, 34.74; H, 2.59; Br, 41.50.

(c) The dienone **2** was treated with methyl orthoformate using the conditions reported in literature.[8] Spectroscopic identification of the reaction product failed to reveal the presence of acetal **1**.

Registry No.—**1**, 24742-01-6; **1** (acetate), 24742-02-7; **3**, 24742-03-8; **4**, 24744-57-8; **5a**, 24744-58-9; **5b**, 24744-59-0; **6**, 24744-60-3; **10** (acetate), 24744-61-4.

Acknowledgment.—This work has been supported in part by National Institutes of Health Grant GM-11735 and in part by Sea Grant Project GH-16.

(8) L. F. Feiser and M. Feiser in "Reagents for Organic Synthesis," John Wiley and Sons, Inc., New York, N. Y., 1967, pp 1206–1207.

Synthesis of Secondary Amines *via* Triphenylphosphinimines

HANS ZIMMER, MADHUSUDAN JAYAWANT,[1] AND PAUL GUTSCH[1]

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

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In continuation of our investigation utilizing triphenylphosphinimines (I) as tools in organic and inorganic synthesis,[2a–c] we investigated further the use of I in the preparation of mixed secondary amines. Our attention was mainly directed toward (a) the synthesis of secondary amines containing a cycloalkyl group and (b) establishing the scope and limitations of this method for the preparation of such amines. The synthesis followed the sequence of reactions of eq 1 and 2.

$$Ph_3\overset{+}{P}-\overset{-}{N}R \longleftrightarrow Ph_3P{=}NR + R'X \longrightarrow [Ph_3P{-}NRR']^+X^- \quad (1)$$

$$[Ph_3PNRR']^+X^- \xrightarrow{H_2O} Ph_3P{=}O + HNRR'^+X^- \quad (2)$$

R = Me, Et, *n*-Pr, *i*-Pr, *i*-Bu, *t*-Bu, 1-Adamantyl
R′ = Me, Et; X = I, Cl, Br

No difficulties were encountered in preparing the corresponding I with R = cyclopropyl, -pentyl, -hexyl, -heptyl, and adamantyl. However, again as reported previously,[2a] only MeI and EtI could be added according to eq 1. Use of any higher alkyl groups, including cyclopropyl, resulted in HX elimination from the alkyl halide and yielded alkylaminotriphenylphosphonium halides according to eq 3.

$$Ph_3P{=}NR + R'X \longrightarrow [Ph_3P{-}NHR]^+X^- + \text{olefin}^{2d} \quad (3)$$

R′ = any C_3 and higher alkyl; X = I

Alkylaminotriphenylphosphonium halides needed for the preparation of I were obtained by treating triphenyldibromophosphorane with the corresponding alkylamine in the presence of triethylamine.[2a,3] Dehydrohalogenation of these phosphonium salts was easily accomplished by treatment with sodium amide in liquid ammonia.[2a] The resulting triphenylphosphinecycloalkylimines were very sensitive to moisture and were used without further purification for the subsequent syntheses. These were carried out according to eq 1 by refluxing the corresponding triphenylphosphinimines in excess alkyl halide. Data on the resulting compounds are compiled in Table I.

All the dialkylaminophosphonium iodides obtained could be hydrolyzed as shown in eq 2. The mixed secondary amines were formed in good yields and were characterized as hemioxalates. Pertinent data are reported in Table II.

In conclusion it can be stated that alkyl addition to triphenylalkylphosphinimines, to give after hydrolysis mixed secondary amines, is limited to addition of methyl and ethyl groups.

Experimental Section

Melting points are uncorrected. Microanalysis was performed by A. Bernhardt, Mikroanalytisches Laboratorium im Max-Planck-Institut, Mülheim/Ruhr, Germany, and by Galbraith Laboratories, Knoxville, Tenn.

Cycloalkylaminotriphenylphosphonium Bromides.—To an ice-cooled suspension of triphenyldibromophosphorane (0.1 mol) in benzene was slowly added a solution of triethylamine (0.1 mol) and the appropriate cycloalkylamine (0.1 mol) in 50 ml of dry benzene. The reaction was stirred for 3 hr before filtering. The collected precipitate was washed with ether and then with ice water. After drying it was dissolved in 100 ml of chloroform, treated with Norit, and filtered. Excess anhydrous ether (200 ml) was added to the chloroform solution and the precipitated bromide was filtered off. The mother liquors yielded a second crop on refrigerating overnight. The cycloalkylaminotriphenylphosphonium bromides were recrystallized from chloroform–ether to give analytically pure samples.

Cyclopropylaminotriphenylphosphonium bromide: yield 82%; mp 204°. *Anal.* Calcd for $C_{21}H_{21}BrNP$: C, 63.31; H, 5.31; N, 3.52. Found: C, 63.10, H, 5.34; N, 3.50.

Cyclopentylaminotriphenylphosphonium bromide: yield 89%; mp 188°. *Anal.* Calcd for $C_{23}H_{25}BrNP$: C, 64.79; H, 5.91; N, 3.29. Found: C, 65.27; H, 5.96; N, 3.35.

Cycloheptylaminotriphenylphosphonium bromide: yield 85%; mp 194–195°. *Anal.* Calcd for $C_{25}H_{29}BrNP$: C, 66.07; H, 6.43; N, 3.08. Found: C, 66.14; H, 6.22; N, 3.24.

Adamantylaminotriphenylphosphonium Bromide: yield 79%; mp 261–263°. *Anal.* Calcd for $C_{28}H_{31}BrNP$: N, 6.30. Found: N, 6.32.

Triphenylphosphinecycloalkylimines.—To a stirred suspension of the appropriate cycloalkylaminotriphenylphosphonium bromide (0.05 mol) in anhydrous ammonia was added 2.2 g of sodium amide (0.055 mol) and the resulting mixture was stirred for 1 hr in a Dry Ice–acetone bath. Ammonia was then evaporated by removing the cold bath and continuing the stirring. The solid remaining in the flask was extracted repeatedly with anhydrous ether. Evaporation of the combined extracts gave the desired phosphinimines which were recrystallized from anhy-

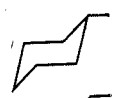
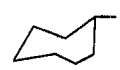
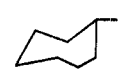
(1) M. Jayawant, Ph.D. Thesis, University of Cincinnati, Cincinnati, Ohio, 1967, and P. Gutsch, 1970, respectively.

(2) (a) H. Zimmer and G. Singh, *J. Org. Chem.*, **28**, 483 (1963); (b) H. Zimmer and G. Singh, *Angew. Chem., Int. Ed. Engl.*, **2**, 395 (1963); (c) H. Zimmer and G. Singh, *J. Org. Chem.*, **29**, 3412 (1964). (d) The olefins were qualitatively identified by decolorization of bromine–water reagent. The stoichiometry and exact mechanism of the olefin forming reaction are presently being investigated.

(3) L. Horner and H. Hoffmann, *Angew. Chem.*, **68**, 473 (1956).

TABLE I

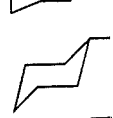
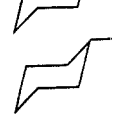
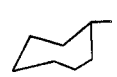
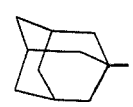
$$[(C_6H_5)_3P{=}NR + R'I \longrightarrow \left[(C_6H_5)_3\overset{+}{P}-N\begin{matrix}R'\\ \\ R\end{matrix}\right] I^{-a}$$

Compd no.	R	R′	Formula	Mol wt	Mp,[b] °C	Yield, %	C, % Calcd	C, % Found	H, % Calcd	H, % Found	N, % Calcd	N, % Found
1		CH_3	$C_{22}H_{23}INP$	459.29	211–212	85.7	57.51	57.47	5.05	5.06	3.05	30.4
2		C_2H_5	$C_{23}H_{25}INP$	473.32	234–235	78.2	58.34	57.69	5.32	5.19	2.96	3.01
3		CH_3	$C_{24}H_{27}INP$	487.35	234–235	87.5	59.16	59.05	5.59	5.60	2.87	3.01
4		C_2H_5	$C_{25}H_{29}INP$	501.37	183–184	75.6	59.84	59.23	5.83	5.66	2.79	3.06
5		CH_3	$C_{25}H_{29}INP$	501.37	248–249	78.2	59.84	59.98	5.83	5.54	2.79	2.78
6		C_2H_5	$C_{26}H_{31}INP$	515.42	186–187	70.0	60.59	60.91	6.06	5.84	2.72	2.84
7		CH_3	$C_{26}H_{31}INP$	515.42	237–238	75.4	60.59	60.01	6.06	6.13	2.72	2.91
8		C_2H_5	$C_{27}H_{33}INP$	529.44	201–202	68.3	61.25	61.25	6.28	6.14	2.64	2.20
9		CH_3	$C_{29}H_{33}INP$	553.46	271–272	95.5	62.95	63.03	5.97	6.35	2.54	2.59

[a] Crystallized from $CHCl_3$–ether. [b] Melting points are uncorrected.

TABLE II

$$\left[(C_6H_5)_3\overset{+}{P}-N\begin{matrix}R\\ \\ R'\end{matrix}\right] I^- \xrightarrow[2.\ \text{anhydrous } (COOH)_2]{1.\ \text{alcoholic KOH}} [RR'NH_2]^+[OOC{-}COOH]^-$$

Compd no.	R	R′	Formula	Mol wt	Yield,[a] %	Mp,[b] °C	C, % Calcd	C, % Found	H, % Calcd	H, % Found	N, % Calcd	N, % Found
1		CH_3	$C_6H_{11}NO_4$	161.16	76.3	110–111	44.71	44.77	6.88	7.12	8.69	8.74
2		C_2H_5	$C_7H_{13}NO_4$	175.18	74.0	169–170	47.99	48.04	7.48	7.61	8.00	8.11
3		CH_3	$C_8H_{15}NO_4$	189.21	68.7	119.5–120.5	50.78	50.65	7.99	8.17	7.40	7.40
4		C_2H_5	$C_9H_{17}NO_4$	203.23	71.8	137–138	53.19	53.06	8.43	8.38	6.89	7.10
5		CH_3	$C_9H_{17}NO_4$	203.23	65.5	107.5–108.5	53.19	53.03	8.43	8.17	6.89	7.00
6		C_2H_5	$C_{10}H_{19}NO_4$	217.26	68.6	161–162	55.28	55.64	8.82	8.42	6.45	6.44
7		CH_3	$C_{10}H_{19}NO_4$	217.26	67.0	157–158	55.28	55.38	8.82	8.84	6.45	6.44
8		C_2H_5	$C_{11}H_{21}NO_4$[c]	231.29	69.4	171.5–172.5	57.12	56.92	9.15	8.89	6.06	6.30
9		CH_3	$C_{24}H_{40}N_2O_4$[d] $\times$ 1/2 H_2O	429.58	82.0	221 (d)	67.10	67.25	9.56	9.60	6.53	6.44

[a] Crystallized from ethanol–ether. [b] Melting points are uncorrected. [c] Crystallized from 95% ethanol as hemihydrate. [d] Crystallized as $[RR'NH_2)_2{}^+[OOCCOO]^{2-} \cdot 1/2\ H_2O$

drous hexane. It is mandatory to keep an inert and dry atmosphere over solutions or solids during reactions, isolations, and crystallization.

The crude solids were usually used directly without further purification. The crude phosphinimines could be stored over KOH pellets in a vacuum desiccator without appreciable decomposition.

N-Methylcyclyalkylaminotriphenylphosphonium Iodides (Table I, Compounds 1, 3, 5, 7).—The appropriate triphenylphosphinecycloalkylimine (3–4 g) and 15 ml of methyl iodide were refluxed in an inert atmosphere for 3 hr. To the solution, after cooling, was added sufficient anhydrous ether, whereupon a pale yellow precipitate was deposited. Purification was done by crystallization from chloroform–ether. Yields based on starting phosphinimine were usually high (Table I).

N-Ethylcycloalkylaminotriphenylphosphonium Iodides (Table I, Compounds 2, 4, 6, 8).—These compounds were obtained analogously except that 15 ml of anhydrous *t*-butyl alcohol was used as solvent.

N-Methylcycloalkyl- and N-Ethylcycloalkylammonium Hemioxalates. Hydrolysis of N-Methylcycloalkyl- and N-Ethylcycloalkylaminotriphenylphosphonium Iodides (Table II, Compounds 1–8).—A mixture of 3 g of the appropriate dialkylaminotriphenylphosphonium iodide (*ca.* 0.0055–0.007 mol) and 30 ml of 2% alcoholic potassium hydroxide solution was sealed under an inert atmosphere in a Jena glass pressure bottle and was heated on a steam bath for 3 hr. The bottle then was chilled and carefully opened. The reaction mixture which contained the free amine was saturated with NaCl and was extracted with ether. After combining all ether extracts and drying them over anhydrous sodium sulfate, they were filtered slowly with stirring into a solution of 2 g of anhydrous oxalic acid in 75 ml of dry ether. The white precipitate of hemioxalate which immediately formed was collected, washed with anhydrous ether, and finally purified by recrystallization from ethanol–ether.

Registry No.—Cyclopropylaminotriphenylphosphonium bromide, 24571-65-1; cyclopentylaminotriphenylphosphonium bromide, 24571-66-2; cycloheptylaminotriphenylphosphonium bromide, 24571-67-3; adamantylaminotriphenylphosphonium bromide, 24571-68-4; Table I—**1**, 24571-69-5; **2**, 24571-70-8; **3**, 24571-71-9; **4**, 24571-72-0; **5**, 24571-73-1; **6**, 24571-74-2; **7**, 24571-75-3; **8**, 24571-76-4; **9**, 24571-77-5; Table II—**1**, 24571-78-6; **2**, 24571-79-7; **3**, 24571-80-0; **4**, 24571-81-1; **5**, 24571-82-2; **6**, 24571-83-3; **7**, 24571-84-4; **8**, 24571-85-5; **9**, 24571-86-6.

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Photodimerization of Some Thiophene Analogs of Chalcone

HANS WYNBERG, M. B. GROEN, AND RICHARD M. KELLOGG

Department of Organic Chemistry, The University Bloemsingel, 10, Groningen, The Netherlands

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Since the early work of Stobbe[1,2] concerning the photodimerization of chalcone (benzalacetophenone) and some of its derivatives, this reaction has attracted surprisingly little attention.[3] Recently[4] we established that 1,2-dithienylethenes and 2-styrylthiophene, in contrast to stilbene,[5] failed to undergo photochemical dimerization.[4] It seemed of interest to see if the replacement of a phenyl by a thienyl ring in chalcone would also prevent dimerization. An additional motivation was provided by the fact that dimerization would yield cyclobutanes substituted with thiophene rings. This in turn would open the way to the synthesis of unusual cyclobutanes.[6]

Results

The heterocyclic chalcones **1–3** were readily prepared by the condensation of the appropriate aldehydes and ketones as described in literature.[7]

Concentrated solutions (*ca.* 35% wt/vol) in chloroform were irradiated in ordinary micro test tubes for 20 hr using 350 mμ ("dark light") lamps. In addition to large amounts of resinous material, insoluble in ethanol, colorless soluble compounds which turned out to be the cyclodimers **5–8** were also formed. 3-Phenyl-1-(2-thienyl)-2-propen-1-one (**1**) under the given conditions afforded the dimer **5** in 10% yield, mp 128–129.5° (from ethanol). Similarly, 1-phenyl-3-(2-thienyl)-2-propen-1-one (**2**) gave the cyclobutane derivative **6**, mp 132–134° (from ethanol) in 6–10% yield; 1,3-di-2-thienyl-2-propen-1-one (**3**) furnished in 4% yield a mixture of dimers **7** and **8**, mp 124–134° (from ethanol), in a ratio of about 10:1. The dimeric structure of the compounds was revealed by elemental analysis in combination with molecular weight determinations (osmometric in carbon tetrachloride) and by the spectroscopic properties. In order to elucidate the stereochemistry of the dimers the experiments of Stobbe[1,2] were repeated. Irradiation of a concentrated solution of 1,3-diphenyl-2-propen-1-one (chalcone, **4**) in chloroform in small quartz tubes for 20 hr afforded in 6% yield the dimer **9**, mp 125–126.5° (from ethanol, lit.[2] 124–125°). The reaction was incomplete, however, since considerable starting material remained (as a *cis–trans* mixture) and no resinous polymer was found. When ordinary glass tubes were used, another dimer was formed in extremely low yield upon irradiation of a solution of chalcone for 20 hr. Almost all of the starting material was still present as a *cis–trans* mixture. This dimer **10** (mp 234–236°) was also reported by Stobbe. The dimerizations of **1** and **4** have also been carried out in the presence of iodine, taking longer irradiation times (*ca.* 48 hr). The yields were improved considerably by this procedure; **1** gave a 22% yield of **5**, while **4** furnished the dimer **9** in 28% yield (Scheme I).

Discussion

On inspection of the mass spectra of the photodimers **5** and **6**, it was found that the fragmentation pattern was compatible only with a head-to-head structure.

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(2) H. Stobbe and K. Bremer, *J. Prakt. Chem.*, **123** [2], 1 (1929).
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