diazole (Ij); 2,5-bis-[3,3′-(1,1-didifluoro-2,2-dichloroethoxy)-phenyl]-1,3,4-oxadiazole (Il); 2,5-bis[4,4′-(1,1,2-trifluoro-2-chloroethoxy)phenyl]-1,3,4-oxadiazole (Im); 2,5-bis-[3,3′,5,5′-(1,1,2,2-tetrafluoroethoxy)phenyl]-1,3,4-oxadiazole (In); 2,5-bis-[3,3′,5,5′-(1,1,2-trifluoro-2-chloroethoxy)phenyl]-1,3,4-oxadiazole (Io).

General Procedure Used in the Insecticide Screen. The wild type strain *Drosophila melanogaster*, Oregon-RC, was used in the screening procedure. One hundred *Drosophila* eggs were placed in a 1 × 9 cm vial containing an 8-mL solution of the egg culture media (a standard yeast, corn meal, agar mixture) and the compound to be screened (dissolved or dispersed in soybean oil). Larvacidal kill was the difference between the number of eggs placed on the media and the number of pupae formed. Total kill was the difference between the number of eggs and the number of living adults.

Registry No. Ia, 114467-42-4; Ib, 114467-43-5; Ic, 114467-44-6; Id, 114467-45-7; Ie, 114467-46-8; Ij, 114467-47-9; Il, 114467-48-0; Im, 114467-49-1; In, 114467-50-4; Io, 114467-51-5; IIa, 114467-26-4; IIb, 114467-27-5; IIc, 114467-28-6; IId, 114467-29-7; IIe, 114467-30-0; IIf, 114467-31-1; IIg, 114467-32-2; IIh, 114467-33-3; III, 114467-34-4; IIj, 114467-37-7; IIj (acid), 70126-48-6; IIk, 114467-38-8; IIk (acid), 403-71-4; III, 114467-39-9; III (acid), 114467-35-5; IIm, 114467-40-2; IIm (acid), 405-43-6; IIn, 114467-41-3; IIn (acid), 70126-49-7; IIo, 114490-28-7; IIo (acid), 114467-36-6; 2,4-$Cl_2C_6H_3COCl$, 89-75-8; 4-$(CHF_2CF_2O)C_6H_4CONHNH_2$, 114467-18-4; 4-$(CHClFCF_2O)C_6H_4CONHNH_2$, 114467-19-5; 4-$(CHCl_2CF_2O)C_6H_4CONHNH_2$, 114467-20-8; 3-$(CHF_2CF_2O)C_6H_4CONHNH_2$, 114467-21-9; 3-$(CHClFCF_2O)C_6H_4CONHNH_2$, 114504-85-7; 3-$(CHCl_2CF_2O)C_6H_4CONHNH_2$, 114467-22-0; 3,5-$(CHF_2CF_2O)_2C_6H_3CONHNH_2$, 114467-23-1; 3,5-$(CHClFCF_2O)_2C_6H_3CONHNH_2$, 114467-24-2; 3,5-$(CHCl_2CF_2O)_2C_6H_3CONHNH_2$, 114467-25-3; N_2H_4, 302-01-2.

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A Convenient Synthesis of Amino-Substituted 2-Oxo-1,3,5-triazinium and 1,3,5-Oxadiazinium Salts

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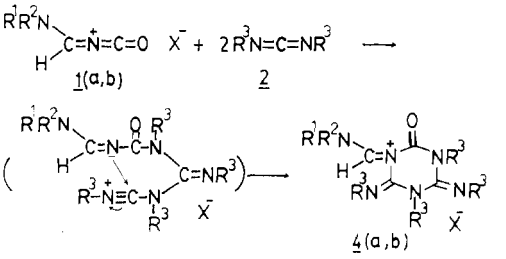
The synthesis of amino-substituted 2-oxo-1,3,5-triazinium hexachloroantimonates 4a,b and amino-substituted 1,3,5-oxadiazinium hexachloroantimonates 5a–h and their spectral data are reported.

In the past few years new classes of heterocumulenes have been synthesized and characterized by Jochims and his coworkers (*1–7*). Especially 1-oxa-3-azabutatrienium salts, **1**, show a wide range of reactivity. As part of our continuing interest in the reactions of these heterocumulenes, I herein report details of the reaction of amino substituted 1-oxa-3-azabutatrienium hexachloroantimonates **1a,b** with diisopropylcarbodiimide (**2**) and dialkylcyanamide **3a–d** to give amino-substituted 2-oxo-1,3,5-triazinium hexachloroantimonates **4a,b** and amino-substituted 1,3,5-oxadiazinium hexachloroantimonates **5a–h**, respectively, in high yields (Schemes I and II). The products are characterized by ^1H NMR, ^{13}C NMR, and IR spectroscopy.

Scheme I. Reactions of 1-Oxa-3-azabutatrienium Salts 1a,b with Diisopropylcarbodiimide (2)



1a: $R^1 = R^2 = CH_3$
1b: $R^1 = CH_3$; $R^2 = C_6H_5$
2: $R^3 = (CH_3)_2CH$
$X = SbCl_6$
4a: $R^1 = R^2 = CH_3$; $R^3 = (CH_3)_2CH$
4b: $R^1 = CH_3$; $R^2 = C_6H_5$; $R^3 = (CH_3)_2CH$

Experimental Section

The melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 299 spectrophotometer. ^1H NMR (250 MHz) and ^{13}C NMR (63 MHz) spectra were determined at 303 K on a Bruker MW-250 instrument in CD_3CN with TMS as internal standard (Table I). Elemental analyses were performed by CHN-microanalyse, Fakulatat Chemie-Universitat Konstanz, FRG. The found elemental analyses for carbon, hydrogen, and nitrogen were in good agreement with those calculated and were submitted for review. All experiments were carried out with exclusion of moisture in absolute solvents.

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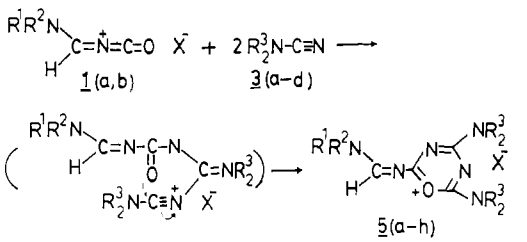
Table I. ^1H and ^{13}C NMR Spectral Data of Compounds 4 and 5

compd	^1H NMR	^{13}C NMR
4a[a]	CH_3 1.20 (d, 6 H, J = 6 Hz), 1.47 (d, 18 H, J = 7 Hz); $(CH_3)_2CH$ 3.98 (m, 2 H), 4.12 (m, 1 H), 4.25 (m, 1 H); NCH_3 3.02 (s, 3 H), 3.45 (s, 3 H); CH 7.86 (s, 1 H)	CH_3 20.7, 21.7, 22.0, 24.5; NCH_3 41.4, 48.2; CH 49.4, 53.6, 56.3, 60.8; C=O, C=N 135.6, 155.1, 156.4, 196.1
4b	CH_3 1.23 (d, 6 H, J = 7 Hz), 1.51 (18 H); $(CH_3)_2CH$ 4.05 (broad, 2 H), 4.19 (broad, 1 H), 4.32 (broad, 1 H); NCH_3 3.72 (s, 3 H); aromatic 7.31–7.56 (m, 5 H); CH 8.14 (s, 1 H)	
5a	NCH_3 3.14 (s, 3 H), 3.16 (s, 3 H), 3.17 (s, 3 H), 3.18 (d, 3 H, J = 1 Hz), 3.23 (s, 3 H), 3.27 (s, 3 H), 3.31 (s, 3 H); CH 8.79 (s, 1 H)	NCH_3 36.7, 36.9 (2 C), 37.6, 37.7, 37.8, 38.0, 43.1; C=O, C=N 157.7, 161.6, 162.8, 163.7
5b[a]	CH_3 1.43–1.30 (24 H); NCH_3 3.19 (d, 3 H, J = 1 Hz), 3.31 (s, 3 H); CH 8.71 (s, 1 H)	CH_3 19.7, 20.5 (broad), 20.8, 20.9 (broad), 21.0; NCH_3 36.6, 43.1; CH 47.9, 48.7 (broad, 2C), 49.4; C=O, C=N 157.5, 160.3, 162.2, 163.4
5c	CH_2 1.68 (m, 12 H); NCH_3 3.18 (s, 3 H); 3.31 (s, 3 H); NCH_2 3.64 (t, 2 H), 3.76 (t, 2 H), 3.84 (t, 2 H), 3.92, (t, 2 H); CH 8.77 (s, 1 H)	CH_2 24.3, 24.7, 25.7, 26.1, 26.5, 26.7; NCH_3 36.9, 43.1; NCH_2 45.9, 46.6, 46.8; C=O, C=N 157.5, 160.3, 162.7, 164.0
5d	NCH_3 3.19 (s, 3 H), 3.32 (s, 3 H); NCH_2 3.72 (m, 8 H); OCH_2 3.89 (t, 4 H), 3.97 (t, 4 H); CH 8.79 (s, 1 H)	NCH_3 37.1, 43.2; NCH_2 45.3, 45.6, 46.1, 46.3; OCH_2 66.4 (2 C), 67.0, 67.1; C=O, C=N 158.3, 161.0, 163.0, 164.1
5e	NCH_3 3.17 (s, 3 H), 3.21 (s, 3 H), 3.24 (s, 3 H), 3.25 (s, 3 H), 3.63 (s, 3 H); aromatic 7.40–7.61 (m, 5 H); CH 9.04 (s, 1 H)	NCH_3 36.8, 37.8, 37.9, 38.0, 44.9; C=O, C=N 158.6, 161.5, 162.5, 164.2
5f[a]	CH_3 1.31–1.46 (24 H); NCH_3 3.63 (d, 3 H, J = 0.6 Hz); $(CH_3)_2CH$ (m, 1 H), 4.55 (broad, 3 H); aromatic 7.41–7.60 (m, 5 H); CH 9.01 (d, 1 H, J = 0.6 Hz)	CH_3 19.7, 20.4, 20.9 (broad), 21.0; NCH_3 37.0; CH 48.2, 49.0 (broad), 49.7; C=O, C=N 157.3, 160.2, 161.9, 163.9
5g	CH_2 1.70 (m, 12 H); NCH_3 3.62 (s, 3 H); NCH_2 3.63–3.90 (m, 8 H); aromatic 7.42–7.58 (m, 5 H); CH 9.02 (s, 1 H)	CH_2 24.4, 24.7, 25.8, 26.1, 26.6, 26.8; NCH_3 37.8; NCH_2 45.9, 46.5, 46.6, 46.7; C=O, C=N 157.1, 159.7, 162.2, 164.6
5h[a]	NCH_3 3.63 (d, 3 H, J = 0.6 Hz); NCH_2, OCH_2 3.68–3.91 (m, 16 H); aromatic 7.46–7.55 (m, 5 H); CH 9.05 (d, 1 H, J = 0.9 Hz)	NCH_3 38.0; NCH_2 45.2, 45.5, 46.1 (2 C); OCH_2 66.4 (2 C), 66.9, 67.1; C=O, C=N 157.9, 160.5, 162.6, 164.6

[a] ^1H and ^{13}C NMR spectra were recorded at 273 K.

Scheme II. Reactions of 1-Oxa-3-azabutatrienium Salts 1a,b with Dialkylcyanamides 3a–d



1a: $R^1 = R^2 = CH_3$
1b: $R^1 = CH_3$; $R^2 = C_6H_5$
3a: $R^3 = CH_3$
3b: $R^3 = (CH_3)_2CH$
3c: $R^3 = -(CH_2)_5-$
3d: $R^3 = -(CH_2)_2-O-(CH_2)_2-$
$X = SbCl_6$

5a: $R^1 = R^2 = R^3 = CH_3$
5b: $R^1 = R^2 = CH_3$; $R^3 = (CH_3)_2CH$
5c: $R^1 = R^2 = CH_3$; $R^3 = -(CH_2)_5-$
5d: $R^1 = R^2 = CH_3$; $R^3 = -(CH_2)_2-O-(CH_2)_2-$
5e: $R^1 = CH_3$; $R^2 = C_6H_5$; $R^3 = CH_3$
5f: $R^1 = CH_3$; $R^2 = C_6H_5$; $R^3 = (CH_3)_2CH$
5g: $R^1 = CH_3$; $R^2 = C_6H_5$; $R^3 = -(CH_2)_5-$
5h: $R^1 = CH_3$; $R^2 = C_6H_5$; $R^3 = -(CH_2)_2-O-(CH_2)_2-$

Amino-substituted 1-oxa-3-azabutatrienium hexachloroantimonates **1a,b** were prepared by a literature procedure (*7*). Diisopropylcarbodiimide and dialkylcyanamides were purchased from Aldrich.

General Procedure for the Preparation of Compounds 4 and 5

1-Oxa-3-azabutatrienium hexachloroantimonates **1a,b** (5.0 mmol) were suspended in anhydrous dichloromethane (10 mL) at −20 °C. Diisopropylcarbodiimide (**2**) (10 mmol) or dialkylcyanamide (**3a–d**) (10 mmol) in anhydrous dichloromethane (10 mL) was added dropwise. The reaction mixture was stirred for few hours at room temperature. The product was precipitated by slow addition of anhydrous ether. The products **4a,b** and **5a–h** were collected and recrystallized from dichloromethane/ether.

1-((Dimethylamino)methylene)-1,2,3,4,5,6-hexahydro-3,5-diisopropyl-4,6-bis(isopropylimino)-2-oxo-1,3,5-triazinium Hexachloroantimonate (4a). Reaction time 2 h, yield 88%, pale yellow prisms, mp 122–125 °C (dec). IR (CH_2Cl_2): 1585, 1690, 1750 cm^{-1}.

1,2,3,4,5,6-Hexahydro-3,5-diisopropyl-4,6-bis(isopropylimino)-1-((methylphenylamino)methylene)-2-oxo-1,3,5-triazinium Hexachloroantimonate (4b). Reaction time 2 h, yield 78%, pale yellow powder, mp 132–135 °C (dec). IR (CH_2Cl_2): 1580, 1660, 1750 cm^{-1}.

4,6-Bis(dimethylamino)-2-(isopropylideneamino)-1,3,5-oxadiazinium Hexachloroantimonate (5a). Reaction time 25 h, yield 84%, fine yellow needles, mp 178–181 °C. IR (CH_2Cl_2): 1550, 1600, 1685 cm^{-1}.

4,6-Bis(diisopropylamino)-2-(isopropylideneamino)-1,3,5-oxadiazinium Hexachloroantimonate (5b). Reaction time 25 h, yield 71%, yellow leaflets, mp 201–203 °C. IR (CH_2Cl_2): 1555, 1650 cm^{-1}.

2-(Isopropylideneamino)-4,6-bis(1-piperidino)-1,3,5-oxadiazinium Hexachloroantimonate (5c). Reaction time 5 h, yield 94%, yellow prisms, mp 210–211 °C (dec). IR (CH_2Cl_2): 1570, 1645 (shoulder), 1660 cm^{-1}.

2-(Isopropylideneamino)-4,6-bis(1-morpholino)-1,3,5-oxadiazinium Hexachloroantimonate (5d). Reaction time 6 h, yield 85%, yellow powder, mp 213–215 °C (dec). IR (CH_2Cl_2): 1575, 1610, 1670 cm^{-1}.

4,6-Bis(dimethylamino)-2-(1-phenylethylideneamino)-1,3,5-oxadiazinium Hexachloroantimonate (5e). Reaction time 2 h, yield 91%, fine yellow needles, mp 214–217 °C (dec). IR (CH_2Cl_2): 1540, 1590, 1685 cm^{-1}.

4,6-Bis(diisopropylamino)-2-(1-phenylethylidene-amino)-1,3,5-oxadiazinium Hexachloroantimonate (5f). Reaction time 6 h, yield 81%, orange prisms, mp 182–184 °C (dec). IR (CH_2Cl_2): 1530, 1560, 1660 cm^{-1}.

2-(1-Phenylethylideneamino)-4,6-bis(1-piperidino)-1,3,5-oxadiazinium Hexachloroantimonate (5g). Reaction time 2 h, yield 85%, fine orange crystals, mp 195–198 °C (dec). IR (CH_2Cl_2): 1530, 1570, 1670 cm^{-1}.

4,6-Bis(1-morpholino)-2-(1-phenylethylideneamino)-1,3,5-oxadiazinium Hexachloroantimonate (5h). Reaction time 3 h, yield 71%, orange prisms, mp 203–204 °C (dec). IR (CH_2Cl_2): 1535, 1575, 1670 cm^{-1}.

Acknowledgment

I thank Professor J. C. Jochims, Konstanz University, FRG, for his helpful discussions and laboratory facilities.

Registry No. **1a**, 104543-29-5; **1b**, 110090-09-0; **2**, 693-13-0; **3a**, 1467-79-4; **3b**, 3085-76-5; **3c**, 1530-87-6; **3d**, 1530-89-8; **4a**, 114943-48-5; **4b**, 114943-50-9; **5a**, 114943-52-1; **5b**, 114943-54-3; **5c**, 114943-56-5; **5d**, 114943-58-7; **5e**, 114943-60-1; **5f**, 114943-62-3; **5g**, 114943-64-5; **5h**, 114943-66-7.

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Synthesis of Some New 2,4-Diaryl-6-(β-phenylvinyl)pyridines via Phenacylpyridinium Bromides

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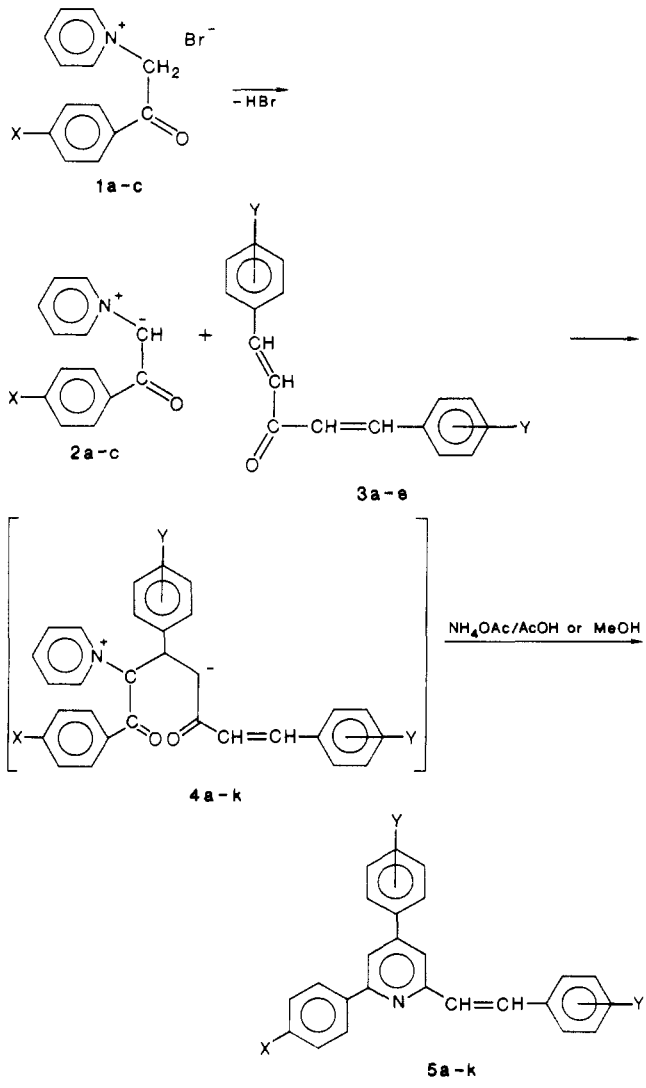
Phenacylpyridinium bromide, *p*-chlorophenacylpyridinium bromide, and *p*-methylphenacylpyridinium bromide were reacted with para-substituted dibenzalacetones in presence of ammonium acetate in glacial acetic acid to give 2,4-diaryl-6-(β-phenylvinyl)pyridines in 45–65% yields. Ammonium acetate in acetic acid was used as an aza cyclization agent. The structures of the resulting pyridines were confirmed by IR and NMR spectral data and elemental analyses.

Pyridinium salts and their ylides have gained considerable importance in the synthesis of indoles (*1*), tetrazine (*2*), pyridines (*3*), and polynuclear hydrocarbon (*4*, *5*). Recently we have studied the synthetic and mechanistic aspects of ylides and their salts of group V elements. We now report herein the reactions of some para-substituted phenacylpyridinium bromides with substituted dibenzalacetones in the presence of ammonium acetate in glacial acetic acid with a view to examine the aza ring closure ability of pyridinium salts with dibenzalacetones (Scheme I).

Scheme I



Experimental Section

Phenacylpyridinium salts (**1a–c**) were prepared by the reaction of substituted phenacyl bromides with pyridine at reflux (*9*, *10*). Substituted dibenzalacetones were prepared by the condensation of acetone with substituted benzaldehydes in the presence of aqueous NaOH solution (*11*).

The IR spectra of pyridines in general showed two characteristic bands in the region 1500 and 1600 cm^{-1} due to stretching vibrations of C=N and C=C of the pyridine nucleus. In the NMR spectra olefin and aromatic protons were observed in the range δ 6.75–7.10 and δ 7.05, respectively.

Preparation of 2,4-Diaryl-6-(β-phenylvinyl)pyridines (5a–k). General Procedure. A mixture of phenacylpyridinium salt (**1a–c**, 3 mmol), ammonium acetate (3 g), and glacial acetic acid (50 mL) was stirred at 80 °C for 2–3 h. The dibenzalacetone (3.3 mmol) in glacial acetic acid (20 mL) was added dropwise during an interval of 1 h. The temperature was raised

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