Hydrogenolysis of 5c (R_2 = CO_2CH_2Ph). Carbamate **5c** (R_2 = CO_2CH_2Ph) (266 mg, 0.866 mmol) was stirred under a hydrogen atmosphere with 30 mg of 5% Pd/C in 6 mL of MeOH for 1 h. The catalyst was removed by filtration over Celite. Evaporation of the solvent gave 150 mg of **6c** (100%) identical with the sample prepared above.

Acknowledgment. The Robert A. Welch Foundation and NATO (Grant No. RG 158.80) are thanked for generous financial support. Dr. David Sawyer is thanked for high-resolution mass spectra.

Registry No. **1a**·Br^-, 83379-65-1; **1b**·Br^-, 83379-66-2; **1c**·Br^-, 83379-67-3; **1d**·Br^-, 70211-56-2; **2a** (isomer 1), 83379-77-5; **2a** (isomer 2), 83461-43-2; **3a**, 83379-68-4; **3b**, 83379-69-5; **3c**, 3597-42-0; **3d**, 66-77-3; **4a**, 83379-70-8; **4b**, 83379-71-9; **4c**, 36112-61-5; **4d**, 86-55-5; **5a**, 83379-72-0; **5b**, 83379-73-1; **5c**, 83379-74-2; **5c** (R_2 = CO_2CH_2Ph), 83379-75-3; **5d**, 72594-62-8; **6a**, 53811-49-7; **6b**, 83379-76-4; **6c**, 5302-77-2; **6d**, 134-32-7; ethyl vinyl ether, 109-92-2; diphenylphosphoryl azide, 26386-88-9.

Degradation of Aminimides Obtained from Enamines and (Ethoxycarbonyl)nitrene

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Recently, during our ongoing study of nitrene chemistry, we have found a very high ratio of addition to insertion product in the reaction of (ethoxycarbonyl)nitrene (EtOCON) with vinyl chlorides, as compared with the case of other unsubstituted olefins.[1] Aziridines are also the main products in the reaction of $EtOCON_3$ with enol ethers[2] and enol acetates.[3]

We have now extended our study of nitrene reactions to enamines. There are few examples of reactions between nitrenes and amines in the literature. Tertiary amines gave isolable or supposed N–N ylides (aminimides) by addition of electron-deficient nitrene to the nonbonded electron pair.[4] Enamines were, therefore, an interesting substrate for testing the preference of the nitrene to add to the double bond or to the electron pair to give substituted aziridines or aminimides, respectively.

We considered 1-(1-cyclopentenyl)piperidine (**2**), 1-(1-cyclohexenyl)piperidine (**6**), 1-(1-cyclopentenyl)pyrrolidine (**9**), and 1-(1-cyclohexenyl)pyrrolidine (**12**). EtOCON was generated by α elimination from *N*-[[(4-nitrophenyl)-sulfonyl]oxy]urethan (NBSU, **1**) at room temperature.[5] The procedure was modified by adding a threefold excess of triethylamine to the solution of enamine in dichloromethane and then NBSU (**1**) portionwise, during 1 h.

The piperidine enamines **2** and **6** gave the corresponding aminimides (**3** and **7**) in 24% and 33% isolated yields, along with minor amounts of *N*-(ethoxycarbonyl)-2-aminocycloalkanones (**4** and **8**) and 1-[(ethoxycarbonyl)-amino]piperidine (**5**). Under the same conditions, the enamines containing the pyrrolidine ring gave lower yields of the expected aminimides and comparable or higher amounts of **4**, **8**, and 1-[(ethoxycarbonyl)amino]pyrrolidine (**11**). We were never able to isolate the primary product of the nitrene addition to the carbon–carbon double bond, while in the reaction of enamines and dichlorocarbene this was the only isolable product, and it was often stable[6] (Scheme I and experiment a of Table I).

Interestingly, when the reaction on **12** was run without triethylamine (experiment b of Table I), the basic function was fulfilled by the enamine itself, and we found only **8** and **11** (in almost a 1:1 ratio), which seemed thus to be generated from the protonated enamine. In fact, *N*-

Scheme I. Reaction of Enamines NBSU (1) and Et_3N in Dichloromethane at Room Temperature

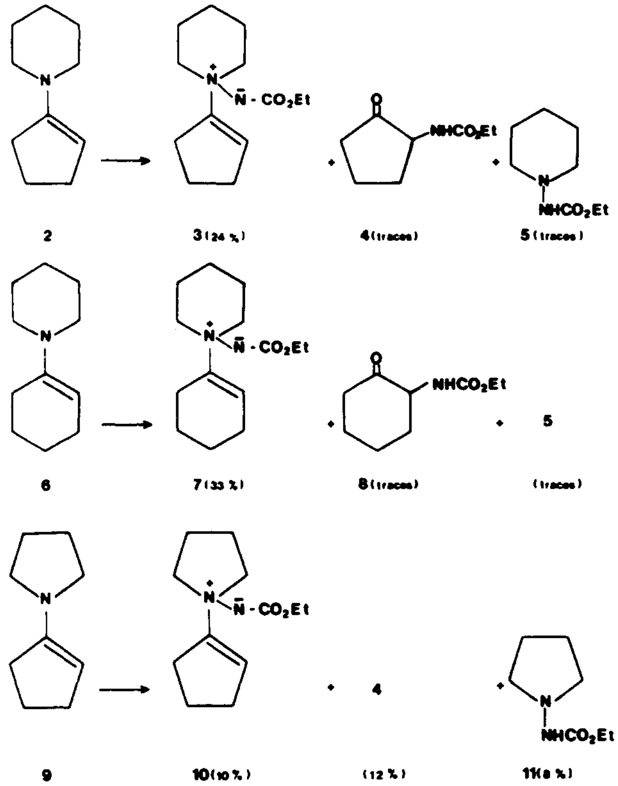
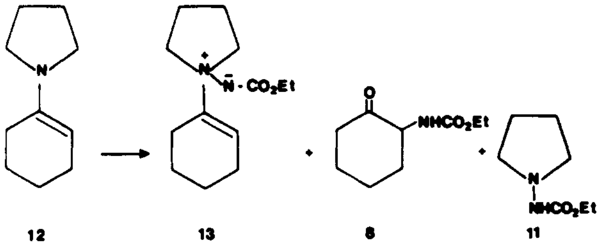


Table I. Reaction of 1-(1-Cyclohexenyl)pyrrolidine (12) or *N*-Cyclohexylidenepyrrolidinium Perchlorate (14) and NBSU (1) in Dichloromethane at Room Temperature under Varied Reaction Conditions



expt	molar ratio	rel yield, % 13	 8	 11
a	1:3 enamine/Et_3N	11	32	57
b	without Et_3N		49	51
c	1:3 perchlorate/Et_3N		36	64
d	1:10 enamine/Et_3N	58	30	12

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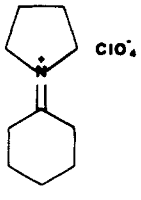
(6) (a) Ohno, M. *Tetrahedron Lett.* **1963**, 1753. (b) Wolinsky, J.; Chan, D.; Novak, R. *Chem. Ind. (London)* **1965**, 720. (c) Bergman E. *J. Org. Chem.* **1963**, *28*, 2210.

cyclohexylidenepyrrolidinium perchlorate (**14**),[7] exposed to similar reaction conditions, gave again **8** and **11** (experiment c of Table I).



14

At this point, it is noteworthy that the thermolysis and photolysis of ethyl azidoformate in cyclohexanone afforded **8** together with several other products in comparable amounts,[8] while EtOCON generated by α elimination in the presence of cyclohexanone gave only the abstraction product *N*,*N*′-bis(ethoxycarbonyl)hydrazine ($EtOCONHNHCO_2Et$). In the presence of pyrrolidine, three products could be detected, **11** and two different compounds, in comparable amounts, the structures of which were not determined. No other products were obtained in the presence of an equimolar mixture of cyclohexanone and pyrrolidine. On the other hand, if the same reaction was accomplished with a large excess of triethylamine (experiment d of Table I), the major product became the aminimide **13**.

In conclusion, the experimental picture reported above should support the involvement of EtOCON, at least as far as the formation of aminimides is concerned. Alternative nonnitrene pathways may be considered to account for the main products (typically **8** and **11**) formed with enamine in the absence of added base, namely, a nucleophilic attack by the anion $EtOCON^-OSO_2C_6H_4$-*p*-NO_2 or an electrophilic amination by NBSU via direct displacement by enamine on the nitrogen atom of NBSU, followed by proton transfer. The last hypothesis should be ruled out in the case of the reaction with perchlorate **14**.

On being allowed to stand at room temperature for several days as well as at lower temperatures for longer times, both aminimides **3** and **10**, containing a cyclopentene moiety, underwent a quantitative transformation into 1-[(ethoxycarbonyl)amino]pyrrolidine (**11**) or 1-[(ethoxycarbonyl)amino]piperidine (**5**), respectively. The aminimides **7** and **13** were instead more stable; actually it was necessary to heat them overnight at 105 °C in 2 N HCl (sealed tube) in order to convert **7** into **5** and **13** into **11**. The cycloalkenyl moiety was found in all cases as the corresponding ketone (cyclopentanone and cyclohexanone, respectively).

The lability and the reactions of **3**, **7**, **10**, and **13** appear novel since a known behavior of structurally similar aminimides is the Wawzonek rearrangement, while heating in acids gives the cleavage of the amidic bond.[9] On the other hand, an analogy can be envisaged with the recently reported results on the transformation of related enammonium salts.[10]

Experimental Section

GC analyses were performed on a Carlo Erba Fractovap GI gas chromatograph with a column of 2% OV-17 (2 m × 2 mm). GC/MS was done, on an AEI MS-12 spectrometer, at an ionization potential of 70 eV, coupled to a Varian 1400 gas chromatograph with a column of 2% OV-17 (2 m × 2 mm). ^1H NMR spectra were recorded on a Perkin-Elmer R 32 90-MHz spectrometer and on a JEOL C 60 HL spectrometer with Me_4Si as an internal standard. Infrared spectra were obtained on a Perkin-Elmer 257 Infracord instrument. Melting points were determined on a Kofler block; melting points and boiling points are uncorrected. NBSU (**1**),[5] 1-(1-cyclopentenyl)piperidine (**2**), 1-(1-cyclohexenyl)piperidine (**6**), 1-(1-cyclopentenyl)pyrrolidine (**9**), and 1-(1-cyclohexenyl)pyrrolidine (**12**) were prepared by standard procedures. Dichloromethane was distilled on $CaCl_2$. Triethylamine was dried by allowing it to stand over activated alumina and then was distilled from calcium hydride.

General Procedure of the Reaction of NBSU (1) with Enamines. To a stirred solution of 10 mmol of enamine, 30 mmol of triethylamine, and 20 mL of dichloromethane in an atmosphere of N_2 was added 10 mmol of **1** in 1 h. After 2 h more of stirring, petroleum ether (bp 30–50 °C) was added, and the precipitate thus formed was filtered off (77–95%). The filtrate was concentrated in vacuo, and the residue was chromatographed on silica gel with a mixture of benzene and ethyl acetate (8:2). A good separation was always obtained, and a complete reverse order of elution was found with respect to the GC retention times.

With 1-(1-Cyclopentenyl)piperidine (2). With **2** as the starting material a 24% yield of **3** was collected together with minor amounts of **4** and **5**.

3: IR (CCl_4) 1720, 1650 cm^{-1}; ^1H NMR (CCl_4) δ 1.3 (t, 3 H, CH_3), 1.4–2.8 (m, 12 H), 3.05 (m, 4 H, CH_2–N), 4.15 (q, 2 H, CH_2–O), 5.35 (m, 1 H, vinylic); mass spectrum, *m/z* (relative intensity) 238 (M$^+$, 13), 166 (36), 84 (100), 82 (37), 67 (13), 55 (42), 44 (62), 41 (38).

4: bp 105 °C (2.5 mm); IR (CCl_4) 3410, 1735 cm^{-1}; ^1H NMR (CCl_4) δ 1.2 (t, 3 H, CH_3), 1.35–2.7 (m, 6 H), 4.05 (q + m, 3 H, CH–N + CH_2–O), 5.4 (br, 1 H, NH); mass spectrum, *m/z* (relative intensity) 171 (M$^+$, 19), 143 (7), 115 (100), 82 (11), 56 (26), 43 (56).

5 [purified by sublimation at 60 °C (3 mm)]: mp 86–87 °C (lit.[11] mp 84–86 °C); IR (CCl_4) 3430, 1740 cm^{-1}; ^1H NMR (CCl_4) δ 1.2 (t, 3 H, CH_3), 1.2–1.9 (m, 6 H), 2.8 (m, 4 H, CH_2–N), 4.05 (q, 2 H, CH_2–O), 6.15 (br, 1 H, NH); mass spectrum, *m/z* (relative intensity) 172 (M$^+$, 22), 99 (100), 90 (10), 84 (82), 87 (73), 82 (36), 70 (10), 62 (10), 55 (68). All spectroscopic data as well as GC retention time were coincident with those of an authentic specimen of **5** prepared according to reported procedure.[11]

With 1-(1-Cyclohexenyl)piperidine (6). With **6** as the starting material a 33% yield of **7** was collected, together with trace amounts of **8**[8] and **5**.

7: IR (CCl_4) 1725 cm^{-1}; ^1H NMR (CCl_4) δ 1.2 (t, 3 H, CH_3), 1.35–2.2 (m, 14 H), 3.0 (m, 4 H, CH_2–N), 4.05 (q, 2 H, CH_2–O), 5.4 (m, 1 H, vinylic); mass spectrum, *m/z* (relative intensity) 252 (M$^+$, 21), 179 (26), 140 (12), 96 (38), 84 (100).

With 1-(1-Cyclopentenyl)pyrrolidine (9). With **9** as the starting material three products were collected: **10** (10%), **4** (12%), and **11** (8%).

10: IR (CCl_4) 1725, 1660 cm^{-1}; ^1H NMR (CCl_4) δ 1.25 (t, 3 H, CH_3), 1.5–2.0 (m, 6 H), 2.1–2.7 (m, 4 H, allylic), 3.05 (m, 4 H, CH_2–N), 4.1 (q, 2 H), 5.35 (m, 1 H, vinylic); mass spectrum, *m/z* (relative intensity) 224 (M$^+$, 10), 155 (30), 151 (30), 126 (30), 116 (27), 110 (36), 96 (18), 82 (100), 70 (43), 69 (40), 68 (37), 67 (34), 66 (30), 55 (43), 54 (43), 44 (68), 41 (82).

11: mp 63–64 °C (lit.[11] mp 64.5–65 °C); IR (CCl_4) 3440, 1735 cm^{-1}; ^1H NMR (CCl_4) δ 1.2 (t, 3 H, CH_3), 1.6–1.9 (m, 4 H), 2.9 (m, 4 H, CH_2–N), 4.0 (q, 2 H, CH_2–O), 5.7 (br, 1 H, NH); mass spectrum, *m/z* (relative intensity) 158 (M$^+$, 10), 85 (100), 70 (75), 41 (18).

With 1-(1-Cyclohexenyl)pyrrolidine (12). With **12** as the starting material three products were collected: **13** (22%), **8** (14%), and **11** (20%).

13: bp 160 °C (2.5 mm); IR (CCl_4) 1725 cm^{-1}; ^1H NMR (CCl_4) δ 1.2 (t, 3 H, CH_3), 1.5–2.3 (m, 12 H), 3.05 (m, 4 H, CH_2–N), 4.05 (q, 2 H, CH_2–O), 5.4 (m, 1 H, vinylic); ^1H NMR (CF_3CO_2H) δ 1.35 (t, 3 H), 1.6–2.1 (m, 4 H), 2.1–2.8 (m, 6 H), 3.2–4.7 (m + q, 9 H), 6.25 (m, 1 H); mass spectrum, *m/z* (relative intensity) 238 (M$^+$,

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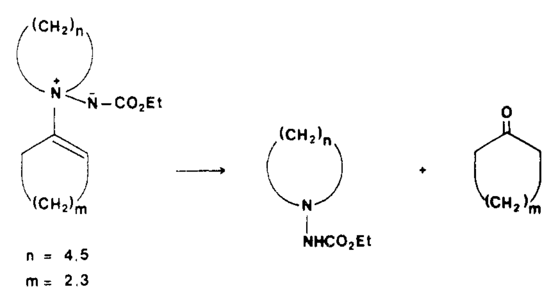
Scheme II. Degradation of Aminimides



23), 169 (23), 165 (46), 140 (46), 96 (100), 70 (69), 69 (46), 55 (23), 41 (38).

***N*-Cyclohexylidenepyrrolidinium perchlorate (14)** was obtained as white crystals by treating **12** with 70% $HClO_4$: mp 228–229 °C (lit.[7] mp 228–229 °C); IR (Nujol) 1670 cm^{-1} (lit.[7] IR 1669 cm^{-1}).

Reaction of NBSU (1) with 14. The general procedure described for the enamines was followed, and the crude reaction mixture was analyzed by GC/MS; after a first peak identified as cyclohexanone, two further peaks were identified as **8** and **11**.

Reaction of NBSU (1) with Cyclohexanone. The general procedure described for the enamines was followed, and the only product recovered other than starting ketone was identified as *N,N'*-bis(ethoxycarbonyl)hydrazine.[12]

Reaction of NBSU (1) with Pyrrolidine. The general procedure described for the enamines was followed, and the crude reaction mixture was analyzed by GC. Three peaks were found, the latter of which was coincident with **11**. GC/MS confirmed the identity. No further investigation of the structures of the other two products was carried out.

Reaction of NBSU (1) with Cyclohexanone and Pyrrolidine in an Equimolar Ratio. The general procedure described for the enamines was followed, and the crude reaction mixture was analyzed by GC, showing the presence of either *N,N'*-bis(ethoxycarbonyl)hydrazine or the three products obtained from pyrrolidine alone.

Degradation of Aminimides. Small aliquots (0.1–0.5 mmol) of the aminimide (**7** or **13**) and 0.5 mL of 2 N HCl were placed in a sealed tube and were heated overnight at 105 °C (see Scheme II). The solution was made alkaline and was extracted with chloroform. The products (**5** or **11**) and cyclohexanone were recognized by GC, IR, ^{1}H NMR, and mass spectra.

Acknowledgment. This work has been financially supported by National Research Council (CNR), Rome; Progetto finalizzato "Chimica fine e secondaria".

Registry No. 1, 2955-74-0; 2, 1614-92-2; 3, 83487-75-6; 4, 83487-76-7; 5, 4663-84-7; 6, 2981-10-4; 7, 83487-77-8; 8, 13640-77-2; 9, 7148-07-4; 10, 83487-78-9; 11, 83487-79-0; 12, 1125-99-1; 13, 83487-80-3; 14, 18448-30-1; EtOCON, 2655-26-7; cyclohexanone, 108-94-1; pyrrolidine, 123-75-1.

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(+)- and (−)-1,1,2,2-Tetrakis(2,6-dimethyl-4-methoxy- and 4-hydroxyphenyl)ethane. First Examples of Optically Active *sym*-Tetraarylethanes: Syntheses, Chiroptical Properties, and Racemization

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1,1,2,2-Tetraarylethanes adopt propeller-shaped ground-state conformations as first had been predicted by force field calculations[1,2] and may therefore be regarded as four-bladed molecular propellers.[3] In these conformations (Figure 1) (a) the ethane hydrogens are in antiperiplanar (ap) positions. (b) the signs of all dihedral angles ϕ (H–C_{ethane}–C_{aryl}–C_{ortho}) are the same (but the geminal aryls are not symmetry equivalent), and (c) tetraarylethanes with four equal aryls have C_2 symmetry and are therefore chiral. For one example (with aryl = phenyl[4]) this special type of chirality has been established in the solid state by X-ray crystal analysis.[5] By NMR spectroscopy the ap conformation in solution can be deduced from an analysis of the ^{13}C satellites of the ^{1}H NMR signal.[4] The feasible symmetries of *sym*-tetraarylethanes with an ap conformation correspond to the point groups C_{2h}, C_2, C_i, C_s, and C_1. A tetraarylethane with eight ortho methyls should display two (C_{2h}), four (C_2, C_i or C_s), or eight (C_1) methyl signals. Since four signals were found for tetraxylylethane[1] and the title compounds **5** and **6**, ground-state conformations C_{2h} and C_1 could be excluded in solution and the ap conformation confirmed by $^3J_{HH}$ measurements (see Experimental Section).

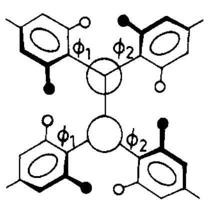
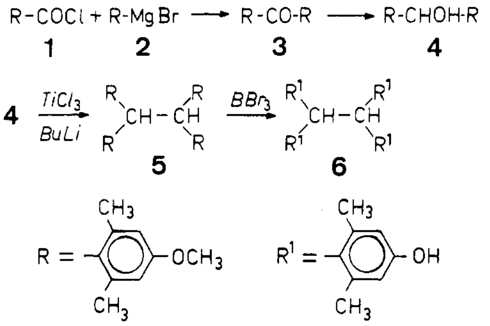


Figure 1. Propeller-shaped conformation of tetraarylethanes.

Scheme I



Results and Discussion

We have now succeeded in resolving the title compounds **5** and **6** thereby obtaining the first examples of optically active *sym*-tetraarylethanes and have therefore furnished the experimental proof for their C_2 symmetry in solution. Moreover, racemization experiments with **5** allowed the determination of $\Delta G^{\ddagger}$ for the racemization process, $\Delta G^{\ddagger}_{20}$ (93 ± 0.5 kJ mol^{-1}), being in good agreement with the value obtained for tetramesitylethane from NMR experiments.[6]

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[3] For a stereochemical discussion on molecular propellers see K. Mislow, *Acc. Chem. Res.* **9**, 26 (1976). Examples for two- and three-bladed molecular propellers are as follows: (a) optically active diarylacetic acids, O. S. Akkerman and J. Coops, *Recl. Trav. Chim. Pays-Bas*, **86**, 755 (1967); (b) perchlorotriphenylamine, K. S. Hayes, M. Nagumo, J. F. Blount, and K. Mislow, *J. Am. Chem. Soc.*, **102**, 2773 (1980).

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