at reflux for 2.25 h. The cooled reaction mixture was diluted with benzene (5 mL), washed, dried, and evaporated. The residue was chromatographed on silica gel with *n*-hexane–benzene (1:4) and then with benzene as eluent to afford 271 mg (47%) of **11**, which was recrystallized from benzene–*n*-hexane to give colorless needles: mp 127–128.5 °C (lit.[3] mp 124–125 °C); NMR ($CDCl_3$) δ 4.71 (d, J = 5.6 Hz, 2, CH_2), 4.92–5.20 (broad, 1, NH), 6.36 (s, 1, H-3), 7.08–7.84 (m, 13, aromatic H); mass spectrum, *m/e* (relative intensity) 346 (M^+, 23), 345 (23), 344 (M^+, 69), 343 (21), 239 (31), 106 (100), 91 (35), 28 (49).

Anal. Calcd for $C_{22}H_{17}ClN_2$: C, 76.62; H, 4.97; N, 8.13. Found: C, 76.51; H, 4.98; N, 7.95.

Acknowledgments. The authors wish to thank Mr. M. Asano for mass spectral measurements and Misses S. Nagasawa and A. Mineo for combustion analyses and NMR spectral measurements, respectively.

Registry No.—**1a**, 67873-09-0; **1b**, 67873-10-3; **1c**, 54567-69-0; **2a**, 22483-09-6; **2b**, 645-36-3; **3a**, 67873-12-5; **3b**, 67873-13-6; **3c**, 67873-14-7; **3d**, 67873-11-4; **4a**, 67873-18-1; **4b**, 67873-15-8; **4c**, 67873-16-9; **4d**, 67873-17-0; **5a**, 2835-77-0; **5b**, 719-59-5; **5c**, 2958-36-3; **6c**, 67873-19-2; **6d**, 67873-20-5; **11**, 51478-50-3; benzylamine, 100-46-9.

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(9) It was confirmed that **3c** was not transformed into the corresponding 4-(2-propoxy) derivative in the UV sample solution by the measurement of the NMR spectrum of the recovered material.
(10) When pure **6** was applied to TLC (silica gel), two spots were observed: one for **6** and the other at the R_f value of the corresponding **3**.

Reactions of Ketene Acetals, Ketene Thioacetals, and Ketene Aminals with Ethyl Benzoylazocarboxylate

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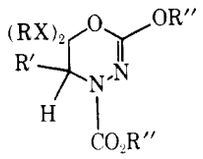
Ethyl benzoylazocarboxylate reacts regiospecifically at room temperature with ketene acetals to give 2-phenyl-4-carboethoxy-6,6-dialkoxy-5,6-dihydrooxadiazines together with varying amounts of 1,1-dialkoxy-2-(*N*-carboethoxy-*N'*-benzoylhydrazinyl)ethylenes. Reaction of ketene thioacetals with ethyl benzoylazocarboxylate gives only the hydrazinylketene dialkyl thioacetals. 1,1-Di(*N*-morpholinyl)ethylene reduces ethyl benzoylazocarboxylate to the dianion and a paramagnetic species, believed to be the cation radical of the aminal.

Diethyl and dimethyl azodicarboxylate esters have been shown to react with ketene acetals, ketene thioacetals, and ketene aminals to give 5,6-dihydrooxadiazines (**1**) and/or hydrazinylketene acetals, hydrazinylketene thioacetals, or hydrazinylketene aminals (**2**).[1] It was shown that in the case



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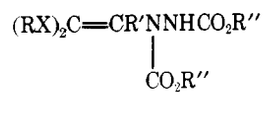
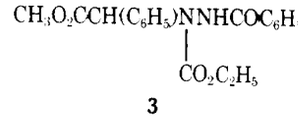


2

of the reactions of phenylketene dimethyl acetal with dimethyl and diethyl azodicarboxylate that the 5,6-dihydrooxadiazine **1** (X = O, R = CH_3, R' = C_6H_5, R'' = CH_3 or C_2H_5) is formed initially but undergoes ring opening and irreversible proton transfer to give the corresponding hydrazinylketene acetal **2**. No 1,2-diazetidines were detected in these reactions. This was surprising, because 1,2-diazetidines have been reported as products in the reactions of azocarboxylate esters with vinyl ethers,[2,4,5,15] vinyl thioethers,[2,6,7] enamines,[2,3,13] vinyl acetates,[2] perfluoroethylenes,[8–10] tetramethoxyethylene,[11] and tetramethoxyallene.[12] The report that 1,2-diazetidines are formed with indene[14] is incorrect.[15,16]

Reaction of ethyl benzoylazocarboxylate with phenylketene dimethyl acetal in benzene at room temperature, followed by chromatography of the reaction mixture on alumina, gave two solids, A and B, mp 88–90 and 116.5–117.5 °C, respectively. Elemental analyses indicated that A was a 1:1 adduct and that B was a hydrolysis product of a 1:1 adduct. Compound A on standing in air or on heating with 5% hydrochloric acid is hydrolyzed to B. Compound B was identified as *N*-(carbomethoxybenzyl)-*N*-carboethoxy-*N'*-benzoylhydrazine (**3**).



3

It was synthesized by reaction of methyl 2-chlorophenylacetate with benzoylhydrazine, followed by acylation of the product with ethyl chloroformate. The samples were shown to be identical (IR, NMR, mixed melting point).

Compounds **4–6** could be reasonably expected to give **3** on hydrolysis and were considered as candidates for compound A. However structure **4** was eliminated by the absence of N–H peaks in the IR and NMR. The NMR spectrum of A contained peaks at 1.30 (t, 3 H), 3.35 (s, 6 H), 4.23 (q, 2 H), 5.72 (s, 1 H), and 7.3–8.1 ppm (m, 10 H). The ultraviolet spectrum of A contained a maximum at 278 nm (ϵ 1.47 × 10^4).

Firl and Sommer studied the reaction of dibenzoyldiimide with styrene, vinyl thioethers, vinyl ethers, and enamines[7] and concluded that the products had the 5,6-dihydrooxadiazine structure, analogous to **6**. Their structural assignments were

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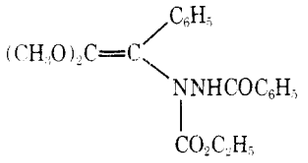

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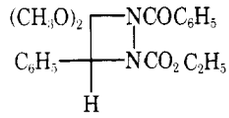

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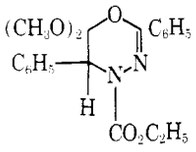
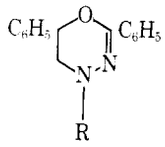
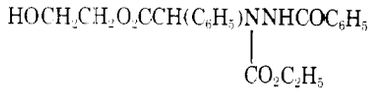


6

based on IR and UV data. They synthesized **7a–c** using a method that could not give 1,2-diazetidines. The UV spectra of **7a–c** and compounds with similar structures were found to exhibit maxima in the range 274–294 nm and ϵ's in range 0.93–2.88 × 10^4. The observation of a maximum at 278 nm and



7a, R = H
b, R = CO_2CH_3
c, R = COC_6H_5



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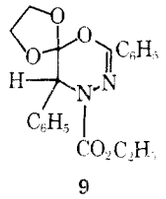
ϵ of 1.47 × 10^4 for compound A is consistent with the 5,6-dihydrooxadiazine structure **6**. It is inconsistent with the 1,2-diazetidine structure **5**, since the model compounds dibenzoyldiimide, dibenzoylhydrazine, and dibenzoyldimethylhydrazine do not have maxima in this region.[17]

The NMR spectrum of **6** exhibited a sharp singlet at 3.35 ppm for the *gem*-dimethoxy groups. The methoxy groups in **6** a priori would not be expected to be equivalent. In 2,6,6-trimethoxy-4-carbomethoxy-5,6-dihydrooxadiazine, the *gem*-methoxy groups appeared as two closely spaced singlets at 3.27 and 3.34 ppm.[1] Either the methoxy groups in **6** accidently have the same chemical shift or they are in some way being averaged.

Compound A exhibited IR peaks at 1705 and 1648 cm^{-1}, which can be assigned to the ester C=O and ring C=N stretching frequencies in the 5,6-dihydrooxadiazine structure **6**. Firl and Sommer[7] reported the ester C=O stretch in the range 1713–1728 cm^{-1} and C=N stretch in the range 1626–1638 cm^{-1} in similar 5,6-dihydrooxadiazines.

When 2-(phenylmethylene)-1,3-dioxolane was reacted with ethyl benzoylazocarboxylate, a 47% yield of compound C, mp 144–145.5 °C, and a 37% yield of compound D, mp 169.5–170.5 °C, were isolated. Hydrolysis of both C and D gave **8**, which is a known compound.[18] Compound C was assigned the 5,6-dihydrooxadiazine structure **9** on the basis of its UV spectrum [283 nm (ϵ 1.70 × 10^4)] and infrared spectrum [1710 (C=O), 1628 (C=N)] and on the basis of the spectral similarity to



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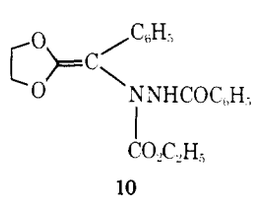
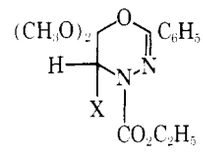


10

compound **6** discussed above. The NMR spectrum exhibited peaks at 1.35 (t, 3 H), 4.31 (m, 4 H), 4.38 (q, 2 H), 5.73 (s, 1 H), and 7.46–8.13 ppm (m, 10 H). The multiplet at 4.31 ppm corresponding to the methylene hydrogens appears almost as a singlet, indicating a high degree of averaging of these hydrogens, similar to the averaging of the *gem*-dimethoxy groups in **6** above.

Elemental analysis of D indicated it was isomeric with **9**. The infrared spectrum [3300, 1640–1750 (broad, unresolved)] indicated the presence of N–H. Accordingly, it was assigned structure **10**. In this case, the methylene multiplet at 4.25 ppm is quite broad rather than sharp as in compound **9**.

Bromoketene diethyl acetal and chloroketene diethyl acetal reacted with ethyl benzoylazocarboxylate. However the products were viscous glasses and defied purification. Nevertheless, examination of the NMR spectra of the glasses strongly suggested that they were mixtures of **11** and **12**. The proton on C-5 in **11a** and **11b** appeared at 6.68 and 6.95 ppm,



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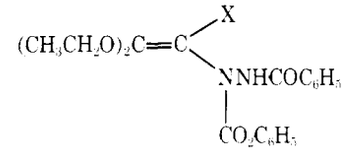
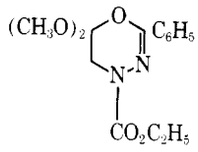


12

a, X = Cl
b, X = Br

respectively. The three nonequivalent ethyl groups of **12a** and **12b** are clearly discernable (likely assignments are given in the Experimental Section). Attempts to purify **11** and **12** by chromatography on alumina in each case gave a low yield of ethyl benzoylhydrazinecarboxylate as the only isolatable product.

When ketene dimethyl acetal was reacted with ethyl benzoylazocarboxylate, a 12% yield of the 5,6-dihydrooxadiazine **13** [IR: 1740, 1705 (C=O), and 1633 (C=N)] as a very viscous oil and a 37% yield of its hydrolysis product **14**, mp 79–80.5 °C,



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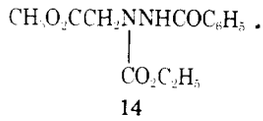
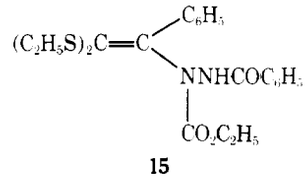


14

were isolated. The C-5 protons in **13** appeared as a singlet at 3.97 ppm and the two methoxy groups as a singlet at 3.50 ppm. Examination of the NMR of the reaction mixture before separation indicated that **13** was the only product formed.

When ethyl benzoylazocarboxylate was reacted with phenylketene diethyl thioacetal, **15** was isolated in 81% yield. The

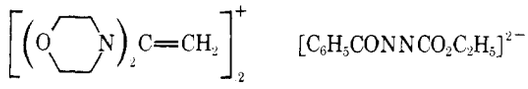


15

structure was assigned on the basis of its three nonequivalent ethyl groups as shown by NMR and the NH at 3320 cm^{-1} in the IR. The carbonyl peaks were in the 1650–1750-cm^{-1} region, but were unresolved. No 5,6-dihydrooxadiazine could be detected in the crude reaction mixture. A similar result was observed in the reactions of ketene thioacetals with dialkyl azodicarboxylates.[1]

When solutions of 1,1-di(*N*-morpholinyl)ethylene and ethyl benzoylazodicarboxylate in benzene were mixed, a violet color appeared. The reaction mixture warmed to 42 °C and the

solution changed color to chocolate brown. After standing 5 days, the reaction mixture was separated on alumina to give a 100% yield of *N*-acetylmorpholine and a 58% yield of ethyl benzoylhydrazinecarboxylate. The chocolate brown solution exhibited an ESR peak at $g = 2.009$. Apparently an initial complex is formed, which dissociates to give a radical. The g factor is very low. One possible candidate for the radical would be the cation **19**, consistent with the known chemistry of ke-



19

tene aminals and tetraaminoethylenes.[19,20] The dianion would account for the formation of the hydrazine on workup. The acetylmorpholine could arise by reaction of water with the cation. It is interesting to note that the dianion of diethyl azodicarboxylate has been described as chocolate brown.[21] The ESR peak showed some evidence of hyperfine splitting. An investigation into the nature of this complex is continuing.

Diethyl and dimethyl azodicarboxylates do not give colored complexes with 1,1-di(*N*-morpholinyl)ethylene, but instead undergo cycloaddition.[1] The LUMO of ethyl benzoylazocarboxylate must therefore be appreciably lower than the LUMO of the dialkyl azodicarboxylates, allowing the reduction process to occur.

The addition of electron-rich ethylenes to azocarboxylate esters can be viewed as a Diels–Alder reaction with inverse electron demand or in the Woodward–Hoffmann terminology as a $\pi 2_s + \pi 4_s$ cycloaddition in which the HOMO of the dienophile delivers electron density to the LUMO of the diene. Using this concept, many of the qualitative observations on the reactions of electron-rich ethylenes with azocarboxylate esters can be correlated. In Figure 1 are listed the energies of the HOMO's and LUMO's of a number of azo compounds and ethylenes from the literature.[22-24]

As can be seen from the figure, the energy of the HOMO's increase in the order of vinyl ether < vinyl thioether < enamine, the order of reactivity which has been observed qualitatively. Likewise the HOMO energy increases in the order ketene acetal < ketene thioacetal < ketene aminal, again in order of the observed reactivity.[1] The energy of the LUMO predicts the reactivity of the azo compounds would be in the order $C_6H_5CON{=}NCO_2R$ > $RO_2CN{=}NCO_2R$ > $C_6H_5N{=}NC_6H_5$. Phenylketene dimethyl acetal failed to react with azobenzene, azoxybenzene, and ethyl phenylazocarboxylate. Phenylketene diethyl thioacetal did not react with azobenzene or azoxybenzene. Ketene dimethyl acetal failed to react with ethyl phenylazocarboxylate. Each of these observations are predictable on the basis of the higher LUMO of the azo compounds. Phenylketene dimethyl acetal reacts 50 times faster with ethyl benzoylazocarboxylate than with diethyl azodicarboxylate, in line with the predicted order.[25]

However, when the energy difference between the HOMO of the dieneophile and the LUMO of the diene becomes low enough, as in the case of the reaction of 1,1-di(*N*-morpholinyl)ethylene and ethyl benzoylazocarboxylate, charge transfer occurs, which in this case is followed by radical cation formation. The observations that tetracyanoethylene forms radical-anion salts with tetrakis(dimethylamino)ethylene,[19,20,26,27] radical cation–radical anion salts with tetramethylthioethylene,[19] and charge-transfer complexes with ketene aminals[28] is consistent with the high energy HOMO's of these ethylenes.

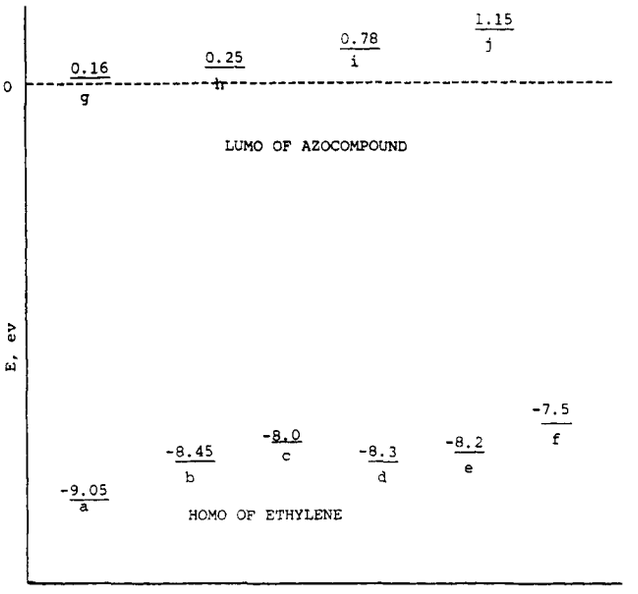


Figure 1. Frontier molecular orbitals of electron-rich ethylenes and electron-poor azo compounds: a, methyl vinyl ether; b, methyl vinyl thioether; c, (dimethylamino)ethylene; d, ketene diethyl acetal; e, ketene dimethyl thioacetal; f, 1,1-bis(dimethylamino)ethylene; g, ethyl benzoylazocarboxylate; h, diethyl azodicarboxylate; i, ethyl phenylazocarboxylate; j, azobenzene, See ref 22–24.

Experimental Section

All boiling and melting points are uncorrected. The infrared spectra were recorded on a Beckman 5A spectrophotometer. The NMR spectra were recorded on a Varian 56/60 spectrometer using Me_4Si as an internal standard. The UV and visible spectra were recorded on a Unicam SP 800 spectrophotometer. The elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn.

Ketene,[29] chloroketene,[30,31] and bromoketene[30] diethyl acetals were prepared by the method of McElvain and Beyerstedt.[30] This method was also adopted to the preparation of phenylketene dimethyl acetal.[32] The method of Boganz and Domasche[33] was used for preparing 1,1-di(*N*-morpholinyl)ethylene. Phenylketene diethyl thioacetal was obtained using the procedure of Rinzema, Stoffelsma, and Arens.[34] The McElvain and Curry[35] method was used to prepare 2-(phenylmethylene)-1,3-dioxolane. Ethyl benzoylazocarboxylate was prepared by oxidation of the hydrazine[36] using the Rabjohn method.[37]

In order to avoid hydrolysis and/or polymerization of the acetals, all glassware was washed with dilute sodium or potassium hydroxide solution and with water, and then thoroughly dried prior to use. The spectroscopic grade benzene used as solvent was dried over sodium for several days. The alumina used in the chromatographic separations was neutral, Brockman Activity 1, 80–200 mesh.

Reaction of Phenylketene Dimethyl Acetal with Ethyl Benzoylazocarboxylate. Ethyl benzoylazocarboxylate (2.666 g, 0.01319 mol) was dissolved in 5 mL of anhydrous benzene and added dropwise to a solution of phenylketene dimethyl acetal (2.163 g, 0.01319 mol) in 5 mL of anhydrous benzene. On mixing, the temperature rose to 36 °C. The reaction mixture was allowed to stand at room temperature for 4 days. The solvent was removed under vacuum.

A portion of the reaction product (2.245 g) was chromatographed on alumina. Elution with benzene gave 1.393 g (62%) of 2,5-diphenyl-4-(carbomethoxy)-6,6-dimethoxy-5,6-dihydrooxadiazine (**6**) as a viscous oil, which exhibited the following spectral characteristics: IR (neat, cm^{-1}) 1705 (C=O), 1648 (C=N); NMR ($CHCl_3$) δ 1.31 (t, 3 H), 3.40 (s, 6 H), 4.27 (q, 2 H), 5.73 (s, 1 H), 7.3–8.1 (m, 10 H); UV ($CHCl_3$) λ_{max} 278 nm (ϵ 1.47×10^4).

In order to further purify the compound, the above oil was rechromatographed. Elution with petroleum ether–ether (3:7) gave two fractions: A, 0.137 g; and B, 0.665 g.

A was the hydrolysis product of the 5,6-dihydrooxadiazine, *N*-(carbomethoxybenzyl)-*N*-carboethoxy-*N'*-benzoylhydrazine (**3**), mp 104–106 °C, and was identical (IR) with the sample prepared below.

B on recrystallization from ether gave **6**, mp 88–90 °C. IR, NMR, and UV spectra were identical with that of the oil above.

Anal. Calcd for $C_{20}H_{22}N_2O_5$: C, 64.85; H, 5.98; N, 7.56. Found: C, 64.88; H, 6.02; N, 7.60.

A second portion of the crude reaction product (0.532 g) was dissolved in 10 mL of ether and stirred at room temperature for 1 h with 10 drops of 5% hydrochloric acid. The solution was dried over mag-

nesium sulfate and chromatographed on alumina. Elution with petroleum ether–benzene (1:3) gave 0.203 g (46.1%) of very viscous oil which solidified on trituration with ether to give pure **3**: mp 116.5–117.5 °C; IR (Nujol, cm^{-1}) 3200 (NH) 1748 and 1710 (C=O); NMR ($CDCl_3$) δ 1.25 (t, 3 H), 3.77 (s, 3 H), 4.21 (q, 2 H), 6.09 (s, 1 H), and 7.42 (m, 11 H).

Anal. Calcd for $C_{19}H_{20}N_2O_5$: C, 64.06; H, 5.61; N, 7.86. Found: C, 63.93; H, 5.80; N, 7.90.

***N*-(Carbomethoxybenzyl)-*N'*-benzoylhydrazine.** Benzoyl hydrazine (1.85 g, 0.0135 mol) was dissolved in 20 mL of absolute methanol and methyl α-chlorophenylacetate (2.5 g, 0.0135 mol) and dried pyridine (1.1 mL) were added. The mixture was refluxed 3 h. The solvent was evaporated and the resulting viscous oil was chromatographed on alumina. Elution with chloroform gave 0.813 g (21.5%) of oily residue, which on trituration with aqueous ethanol gave 0.362 g of pure *N*-(carbomethoxybenzyl)-*N'*-benzoylhydrazine: mp 118–119 °C; IR (Nujol, cm^{-1}) 3215 (NH), 1722 and 1708 (C=O); NMR ($CDCl_3$) δ 3.71 (s, 3 H), 5.00 (s, 1 H), and 7.3–8.0 (m, 11 H).

Anal. Calcd for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.74; H, 5.82; N, 9.90.

***N*-(Carbomethoxybenzyl)-*N*-carboethoxy-*N'*-benzoylhydrazine (3).** *N*-(Carbomethoxybenzyl)-*N'*-benzoylhydrazine (0.362 g, 1.27 mmol) was dissolved in a solvent consisting of 4 mL of ethanol, 2 mL of chloroform, and 1 mL of water. Ethyl chloroformate (0.223 g, 1.27 mmol) was added dropwise with concomitant addition of sodium carbonate (0.0672 g, 0.634 mmol) in 1 mL of water. The mixture was stirred at room temperature for 1 h. The mixture was extracted with chloroform and the extracts were dried over magnesium sulfate. After evaporation of the solvent, the residue was triturated with anhydrous ether to give 0.272 g (60.3%) of the product, mp 112–114 °C. This product was identical (mmp, IR, NMR) with the product obtained by hydrolysis of **6**.

Reaction of Phenylketene Diethyl Thioacetal with Ethyl Benzoylazocarboxylate. Ethyl benzoylazocarboxylate (2.8 g, 0.0136 mol) was dissolved in 5 mL of anhydrous benzene and added dropwise to a solution of phenylketene diethyl thioacetal in 6 mL of anhydrous benzene. The temperature rose from 24 to 27 °C. The reaction was allowed to stand at room temperature for 1 week. The benzene was removed and 2.000 g of the mixture was chromatographed on alumina. The column was eluted with benzene–chloroform (1:3) and then chloroform. Three fractions (1.624 g, 81.1%) were collected, but all three were shown to be identical (IR and NMR). The first two fractions (1.114 g) were rechromatographed. Elution with benzene–chloroform (2:1) gave 0.797 g of pure 1,1-bis(ethylthio)-2-phenyl-2-[*N*-carboethoxy-*N'*-benzoylhydrazinyl]ethylene (**15**) as a viscous oil: IR (neat, cm^{-1}) 3320 (NH), 1740 and 1712 (C=O); NMR ($CDCl_3$) δ 1.12 (t, 3 H), 1.14 (t, 3 H), 1.32 (t, 3 H), 2.65 (q, 2 H), 2.95 (q, 2 H), 4.18 (q, 2 H), and 7.26–7.83 (m, 11 H).

Anal. Calcd for $C_{22}H_{26}N_2O_3S_2$: C, 61.36; H, 6.08; N, 6.50; S, 14.89. Found: C, 61.12; H, 6.02; N, 6.45; S, 14.50.

Reaction of 1,1-Di(*N*-morpholinyl)ethylene with Ethyl Benzoylazocarboxylate. Ethyl benzoylazocarboxylate (3.677 g, 0.0178 mol) was dissolved in 6 mL of anhydrous benzene and added dropwise to a solution of 1,1-di(*N*-morpholinyl)ethylene (3.531 g, 0.0178 mol) in 10 mL of anhydrous benzene. The temperature rose to 42 °C, and the color changed from violet to chocolate brown. The reaction mixture was allowed to stand at room temperature for 5 days. The solvent was removed under vacuum and 1.354 g of the crude reaction mixture was chromatographed on alumina. Elution with benzene–chloroform gave 0.449 g (100%) of *N*-acetylmorpholine: NMR ($CDCl_3$) δ 2.08 (s, 3 H) and 3.62 (m, 8 H). Elution with chloroform and chloroform–ether (7:3) gave 0.405 g (58%) of ethyl benzoylhydrazinylcarboxylate: mp 122–125 °C; mixture melting point gave no depression (pure sample mp 127–128.5 °C).

Reaction of 2-(Phenylmethylene)-1,3-dioxolane with Ethyl Benzoylazocarboxylate. Ethyl benzoylazocarboxylate (2.47 g, 0.0120 mol) was dissolved in 5 mL of anhydrous benzene and added dropwise to a solution 2-(phenylmethylene)-1,3-dioxolane (1.94 g, 0.0120 mol) in 5 mL of anhydrous benzene. The temperature rose to 30 °C. The reaction was allowed to stand at room temperature for 8 days. The benzene was removed under vacuum.

A portion of the residue (1.123 g) was chromatographed on alumina. Elution with benzene–chloroform (3:2) gave fraction A, 0.105 g (9.4%). Elution with benzene–chloroform (1:1) gave fraction B, 0.4229 g (37.6%), and fraction C, 0.381 g (34%). On standing, fractions A and B crystallized. Recrystallization from chloroform gave 0.121 g of the 5,6-dehydrooxadiazine (**9**): mp 144–145.5 °C; IR (Nujol, cm^{-1}) 1710 (C=O) and 1628 (C=N); NMR ($CDCl_3$) δ 1.35 (t, 3 H), 4.3 (m, 6 H), 5.73 (s, 1 H), 7.46–8.13 (m, 10 H); UV (C_6H_5) λ_{max} 283 nm (ϵ 1.70 × 10^4).

Anal. Calcd for $C_{20}H_{20}N_2O_5$: C, 65.20; H, 5.43; N, 7.60. Found: C, 65.08; H, 5.38; N, 7.75.

Trituration of fraction C with anhydrous ether gave 0.120 g (10.7%) of 2-[(*N*-carboethoxy-*N'*-benzoylhydrazinyl)phenylmethylene]-1,3-dioxolane (**10**). Recrystallization from chloroform gave: mp 169.5–170.5 °C; IR (Nujol, cm^{-1}) 3300, (NH) 1640–1750 (unresolved C=O); NMR ($CDCl_3$) δ 1.07 (t, 3 H), 4.08 (q, 2 H), 4.25 (m, 4 H), 7.67–8.47 (m, 11 H).

Anal. Calcd for $C_{20}H_{20}N_2O_5$: C, 65.20; H, 5.43; N, 7.60. Found: C, 65.01; H, 5.32; N, 7.40.

A second portion (0.5817 g) of the crude reaction product was dissolved in 10 mL of ether and stirred at room temperature for 1 h with 10 drops of 5% hydrochloric acid. After drying over magnesium sulfate, the solvent was removed under vacuum. The oily residue was chromatographed on alumina. Elution with chloroform–ethyl acetate (8:2) gave fraction A, 0.1541 g (27.6%), mp 113.5–115 °C, and fraction B, 0.091 g (16.3%), mp 127–130 °C.

Fraction A was identified as 2-hydroxyethyl 2-phenyl-2-(*N*-carboethoxy-*N'*-benzoylhydrazinyl)acetate (**8**): IR (Nujol, cm^{-1}) 3450 (OH), 3340 (NH), 1762, 1725, and 1666 (C=O); NMR ($CDCl_3$) δ 1.27 (t, 3 H), 4.13 (m, 6 H), 6.12 (s, 1 H), 7.47 (m, 10 H), and 8.2 (s, 1 H).

Anal. Calcd for $C_{20}H_{22}N_2O_6$: C, 62.18; H, 5.73; N, 7.14. Found: C, 62.33; H, 5.91; N, 7.39.

Fraction B was identified as *N*-carboethoxy-*N'*-benzoylhydrazine, with which it gave no melting point depression.

Reaction of Bromoketene Diethyl Acetal with Ethyl Benzoylazocarboxylate. Ethyl benzoylazocarboxylate (3.794 g, 0.01872 mol) was dissolved in 5 mL of anhydrous benzene and added dropwise to a solution of bromoketene diethyl acetal in 7 mL of anhydrous benzene. The temperature rose to 36 °C. After standing at room temperature for 2 days, the benzene was removed and the NMR of the residue was obtained. The NMR indicated the presence of two compounds in ca. a 1:1 ratio. 2-Phenyl-4-carboethoxy-5-bromo-6,6-diethoxy-5,6-dihydrooxadiazine (**11b**): NMR ($CDCl_3$) δ 1.37 (t, 8 H), 1.38 (t, 6 H), 3.78 (q, 4 H), 4.45 (q, 2 H), 6.95 (s, 1 H), and 7.41–8.25 (m, 5 H). 1,1-Diethoxy-2-bromo-2-(*N*-carboethoxy-*N'*-benzoylhydrazinyl)ethylene (**12b**): NMR ($CDCl_3$) δ 1.12 (t, 3 H), 1.27 (t, 3 H), 1.38 (t, 3 H), 3.90 (q, 4 H), 4.45 (q, 2 H), and 7.41–8.25 (m, 6 H). The NMR assignments are tentative, in that there was a lot of overlapping peaks. The IR of the mixture showed a band at 3310 cm^{-1} (NH) and multiple carbonyl bands in the 1680–1770-cm^{-1} region. The compounds could not be purified. Attempts to chromatograph the mixture on alumina resulted in decomposition and irreversible retention on the column.

Reaction of Chloroketene Diethyl Acetal with Ethyl Benzoylazocarboxylate. Ethyl benzoylazocarboxylate (1.392 g, 6.965 mmol) was dissolved in 4 mL of anhydrous benzene and added dropwise to a solution of chloroketene diethyl acetal (1.048 g, 6.965 mmol) in 4 mL of anhydrous benzene. After standing 3 days, the benzene was removed under vacuum and the NMR of the residue was examined. The product appears to be approximately a 1:1 mixture of two compounds, **11b** and **12b**. The reaction mixture could not be separated. Attempts to chromatograph the mixture resulted in decomposition and irreversible retention on the alumina. Tentative spectral assignments for the two compounds in the crude reaction mixture are as follows. **11a**: NMR ($CDCl_3$) δ 1.38 (t, 3 H), 1.40 (t, 6 H), 3.42 (q, 4 H), 4.45 (q, 2 H), 6.68 (s, 1 H), 7.41–8.25 (m, 5 H). **12a**: NMR ($CDCl_3$) δ 1.15 (t, 3 H), 1.27 (t, 3 H), 1.38 (t, 3 H), 3.81 (q, 2 H), 4.03 (q, 2 H), 4.25 (q, 2 H), and 7.41–8.25 (m, 6 H). IR of reaction mixture showed a peak at 3330 cm^{-1} (NH), as well as several peaks in the 1680–1770-cm (C=O) region.

Reaction of Ketene Dimethyl Acetal with Ethyl Benzoylazocarboxylate. Ethyl benzoylazocarboxylate (5.550 g, 0.02738 mol) was dissolved in 10 mL of anhydrous benzene and added dropwise to a solution of ketene dimethyl acetal (2.415 g, 0.02738 mol). The temperature rose to 52 °C. After standing at room temperature for 2 days, the benzene was removed.

A portion of the residue (1.440 g) was chromatographed on alumina. Elution with benzene gave 0.1608 g (11.2%) of 2-phenyl-4-carboethoxy-6,6-dimethoxy-5,6-dihydrooxadiazine (**13**) as a viscous oil: NMR ($CDCl_3$) δ 1.40 (t, 3 H), 3.50 (s, 6 H), 3.97 (s, 2 H), 4.38 (q, 2 H); IR (neat, cm^{-1}) 1740, 1705 (C=O), and 1633 (C=N).

Anal. Calcd for $C_{14}H_{18}N_2O_5$: C, 57.13; H, 6.16; N, 9.51. Found: C, 56.99; H, 6.71; N, 9.60.

On standing at room temperature, the dihydrooxadiazine **13** undergoes hydrolysis to give *N*-carboethoxy-*N*-(carbomethoxymethyl)-*N'*-benzoylhydrazine.

Elution of the column with benzene–chloroform (8:2) gave 0.3333 g (23.1%) of *N*-carboethoxy-*N*-(carbomethoxymethyl)-*N'*-benzoylhydrazine: mp 79–80.5 °C (from chloroform); IR (Nujol, cm^{-1})

3330 (NH), 1750, 1716, and 1683 (C=O); NMR ($CDCl_3$) δ 1.25 (t, 3 H), 3.78 (s, 3 H), 4.25 (q, 2 H), 4.51 (s, 2 H).

Anal. Calcd for $C_{13}H_{16}N_2O_5$: C, 55.70; H, 5.75; N, 9.99. Found: C, 55.74; H, 5.71; N, 9.98.

Elution of the column with benzene–chloroform (1:1) gave an additional 0.2051 g (14.3%) of the above hydrazine.

A second portion of the crude reaction mixture (0.8882 g) was dissolved in 10 mL of ether and stirred for 2 h at room temperature with 10 drops of 5% hydrochloric acid. The solution was dried over magnesium sulfate. The ether was evaporated and the residue was chromatographed on alumina. Elution with benzene–chloroform (7:3) gave 0.4010 g (45.1%) of *N*-carboethoxy-*N*-(carbomethoxymethyl)-*N'*-benzoylhydrazine, mp 78–80 °C. This product was identical with the above pure material (IR, NMR, mmp).

Registry No.—3, 67859-20-5; **6,** 67859-21-6; **8,** 67859-22-7; **9,** 67859-23-8; **10,** 67859-24-9; **11a,** 67859-25-0; **11b,** 67859-26-1; **12a,** 67859-27-2; **12b,** 67859-28-3; **13,** 67859-29-4; **14,** 67859-30-7; **15,** 67859-31-8; *N*-(carbomethoxybenzyl)-*N'*-benzoylhydrazine, 67859-32-9; ethyl benzoylazocarboxylate, 10465-85-7; phenylketene dimethyl acetal, 13049-41-7; phenylketene diethyl thioacetal, 66750-44-5; bromoketene diethyl acetal, 42520-11-6; chloroketene diethyl acetal, 42520-09-2; ketene dimethyl acetal, 922-69-0; benzoylhydrazine, 613-94-5; methyl α-chlorophenylacetate, 7476-66-6; ethyl chloroformate, 541-41-3; 1,1-di(*N*-morpholinyl)ethylene, 14212-87-4; *N*-acetylmorpholine, 1696-20-4; ethyl benzoylhydrazinylcarboxylate, 10465-97-1; 2-(phenylmethylene)-1,3-dioxolane, 4362-17-8.

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Notes

2-Fluoro-3-phenyl-2-cyclobutenylidene. Generation via the Bamford–Stevens Reaction and Addition to Olefins

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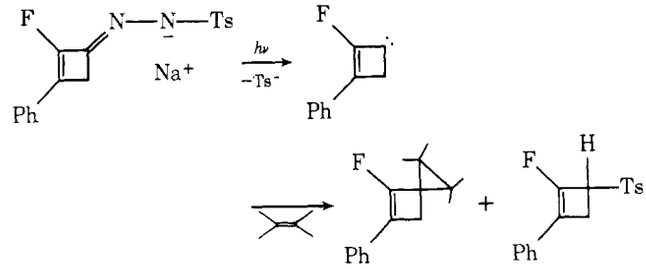
It has been noted that reference to cyclobutenylidene is "conspicuous by its absence from the literature".[1] Only two previous reports pertinent to its chemistry have been noted. Addition to alkenes and alkynes of the species generated by halogen–metal exchange of hexachlorocyclobutene and 3-*H*-pentachlorocylobutene has been found.[2] Unsubstituted cyclobutenylidene, when prepared by deoxygenation of cyclobutenone with atomic carbon, rearranges to vinylacetylene.[3]

While vinylmethylene has been shown by ESR spectroscopy to possess a triplet ground state,[4] the small bond angle at the divalent carbon of cyclobutenylidene and the interaction of the p orbital of the divalent carbon with the π system of the double bond should serve to stabilize the lowest singlet state of cyclobutenylidene.[5] The generation of 2-fluoro-3-phenyl-2-cyclobutenylidene is reported here as well as its stereochemistry of addition and relative reactivity toward several olefins.

2-Fluoro-3-phenyl-2-cyclobutenone was converted to the sodium salt of its tosylhydrazone by standard procedures. When suspensions of the tosylhydrazone salt in olefins were irradiated with ultraviolet light, spirohexenes were formed in high yields, reported in Table I. Irradiation of tosylhydrazone salts in aprotic media has been shown to produce carbenes, via diazoalkanes. Thus we may formulate the transformations as:



Most of the olefin addition products are unstable, darkening within a few hours under air. An adduct of satisfactory analytical purity was obtained only from 1,1-dichloro-2,2-difluoroethylene. The other adducts were characterized spectroscopically immediately after differential precipitation of the only other product detected, the sulfone, which is also pro-

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