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Reactions of Ketene Acetals, Ketene Thioacetals, and Ketene Aminals with Dialkyl Azodicarboxylate Esters

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Ketene acetals react with azodicarboxylate esters to give 5,6-dihydrooxadiazines. However, these compounds are not very stable and undergo thermal ring opening to give hydrazinylketene acetals. No 1,2-diazetidines could be detected in the reactions. If the starting ketene acetal bears no substitutent, the azodicarboxylate ester can react with the hydrazinylketene acetal product to give 2:1 adducts, which have been shown to be either 5-hydrazinyl-5,6-dihydrooxadiazines or dihydrazinylketene acetals. When ketene acetals with allyic hydrogens are used, such as dimethylketene dimethyl acetal, only ene reaction products are formed. When ketene thioacetals reacted with azodicarboxylate esters, the presence of 5,6-dihydrooxadiazines could not be demonstrated. Only ring-opening products, hydrazinylketene thioacetals, could be isolated. In the reactions of ketene aminals with azodicarboxylate esters a low yield of a 5,6-dihydrooxadiazine was isolated in one case; the main products were hydrolysis products of 1:1 adducts. All of the products of these reactions are very moisture sensitive, the acetal linkages undergoing facile hydrolysis to the corresponding open-chain esters.

The thermal addition of ketene acetals to anhydrides,[1] diazonium salts,[2] ketenes,[3-8] acrylate esters,[9] cyanoethylenes,[10,7] acetylenic esters,[10,11] azides,[12-14] isocyanates,[15-20] α,β-unsaturated aldehydes and ketones,[21-25] and nitroso compounds[6,7] has been reported. Ketene thioacetals undergo thermal addition to ketenes,[8] cyanoethylenes,[26] anhydrides,[26] and acetylenic esters.[27] Ketene aminals have been reported to add thermally to ketenes,[28,29] acrylate esters,[30] cyanoethylenes,[10,31-34] isocyanates,[35,36] and cyclopropenones.[37,38] Among these reports there are examples of 2 + 2, 2 + 4, and 1,3-dipolar cycloadditions, formation of substituted ketene acetals, ketene thioacetals, and ketene aminals, as well as adduct formation arising from electron transfer. All of these reactions are interrelated in that all represent the reaction of an electron-rich olefin with an unsaturated electron-poor acceptor.

The reactions of ketene acetals, ketene aminals, and ketene thioacetals with azodicarboxylate esters appear not to have been examined except for the example of Carey and Neergaard[39] indicating that an azodicarboxylate ester undergoes substitution in a ketene thioacetal. However, several related reactions have been examined, including the reaction of azodicarboxylate esters with tetramethoxyethylene,[7] tetramethoxyallene,[6] vinyl ethers,[40-49] vinyl thioethers,[41,45,46] vinyl acetates,[41,47] and enamines.[41,42,46,50]

Ketene acetals, ketene thioacetals, and ketene aminals were all found to react with dimethyl and diethyl azodicarboxylates at room temperature. The reactions were exothermic. The products of these reactions were sensitive to moisture and in some cases only hydrolysis products could be isolated.

When unsubstituted ketene acetals reacted with dimethyl and diethyl azodicarboxylates, both 1:1 and 2:1 adducts were formed. When ketene dimethyl acetal reacted with dimethyl azodicarboxylate, three products, **3a**, **4a**, and **6a**, were isolated in a ratio of 25:3.3:1. The structure of **3a** was proven by independent synthesis by hydrogenation of the carbomethoxyhydrazone of methyl glyoxylate, followed by acylation of the product with methyl chloroformate. The elemental analysis of **4a** was also consistent with the structure **5a** and the diazetidine **7**. However, the NMR of **4a** showed two singlets for the gem methoxy groups at 3.45 and 3.57 ppm, eliminating the symmetrical structure **5a**. The IR of **4a** showed three carbonyl stretching frequencies at 1760, 1750, and 1720 cm^{-1} and a band at 1683 cm^{-1}, characteristic of the C=N stretch in 5,6-dihydrooxadiazenes,[47] eliminating structure **7**.

On standing at room temperature, **4a** is quantitatively transformed into **6a**. This transformation can be monitored by NMR. After heating for 1 h at 40 °C in deuteriochloroform, only **6a** remained. This reaction appears to involve ring opening of the 5,6-dihydrooxadiazine **4a**, presumably through a 1,4-dipolar intermediate to form **5a**, which is very moisture sensitive and hydrolyzes to **6a**. Similarly, the major product, **3a**, most likely arises by hydrolysis of **2a** obtained from ring opening of **1a**.

The reaction of ketene dimethyl acetal with diethyl azodicarboxylate gave the 1:1 adduct **3b** and the 2:1 adducts **5b** and **6b** in a ratio of 1.5:1:1 as estimated from the NMR spectrum of the reaction mixture. Only **3b** could be isolated and purified. Its structure was proven by independent synthesis as described above for **3a**. When this reaction was run in deuterated benzene in the NMR spectrometer, the first identifiable product was the 5,6-dihydrooxadiazine **4b**, as shown by the appearance of the peak at 3.82 ppm, characteristic of C-5 proton. This is followed by the appearance of the hydrazinylketene acetal **5b** as shown by the appearance of singlet at 3.12 ppm for the two methoxy groups. At the same time, the NH peak at 7.32 ppm begins to appear.

When ketene diethyl acetal was reacted with dimethyl and

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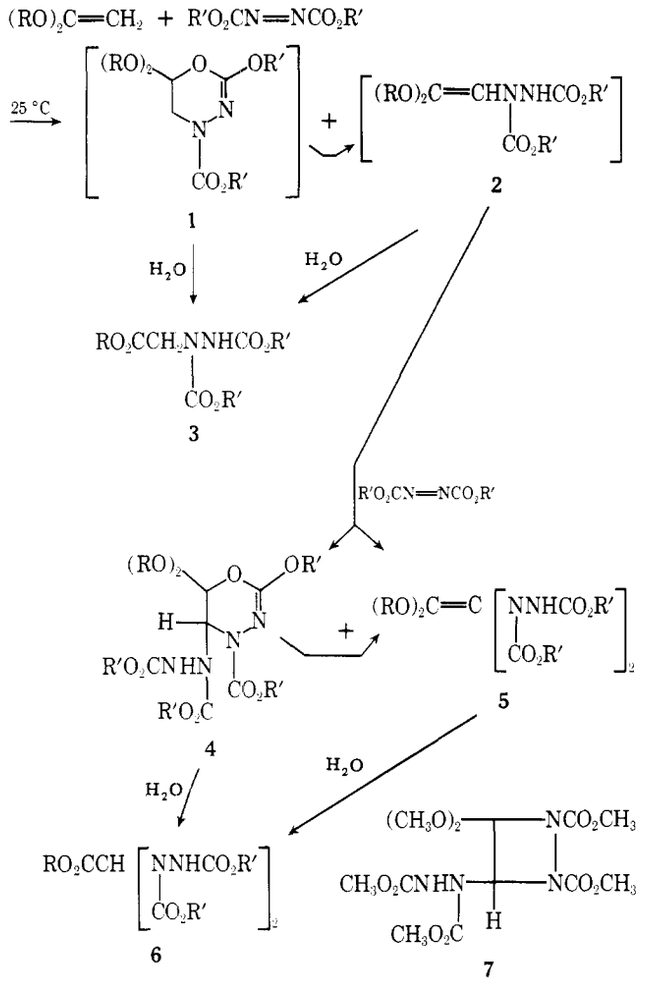
Scheme I



a, R = CH_3; R′ = CH_3
b, R = CH_3; R′ = C_2H_5
c, R = C_2H_5; R′ = CH_3
d, R = C_2H_5; R′ = C_2H_5

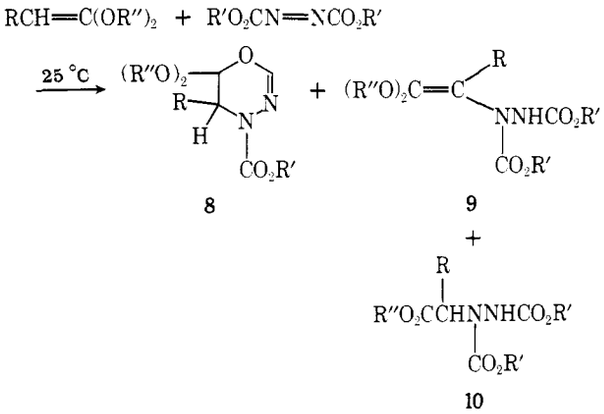
diethyl azodicarboxylates the only products that could be purified were 2:1 adducts **6c** and **6d.**

When chloroketene and bromoketene diethyl acetals were reacted with dimethyl azodicarboxylate, the products were viscous oils (glasses) and attempts to purify them failed. The product from the bromo compound showed an NH stretch at 3290 cm^{-1} and two carbonyl stretching frequencies at 1770 and 1733 cm^{-1} in the IR. The NMR showed two nonequivalent methoxy groups at 3.74 and 3.80 ppm and a singlet at 6.73 ppm corresponding to CHBr. Similarly, the IR of the chloro compound exhibited an N–H at 3300 cm^{-1} and carbonyl frequencies at 1750 and 1730 cm^{-1}, and the NMR showed two nonequivalent methoxy groups at 3.60 and 3.67 ppm and a singlet at 6.43 ppm for CHCl. The spectral information is consistent with the 1:1 hydrolysis products **10a** and **10b.**

Dibromoketene diethyl acetal failed to react with dimethyl azodicarboxylate even when the reaction mixture in benzene was refluxed 67 h.

Phenylketene dimethyl acetal reacts with dimethyl azodicarboxylate to give a mixture of the 5,6-dihydrooxadiazine **8c** and the hydrazinylketene dimethyl acetal **9c** in a 2:1 ratio and with diethyl azodicarboxylate to give **8d** and **9d** in a 5:1 ratio (Scheme II). The 5,6-dihydrooxadiazines **8c** and **8d** showed the characteristic two singlets for the geminal methoxy groups at 3.27 and 3.34 ppm and at 3.28 and 3.36 ppm, respectively, corresponding to the axial and equatorial positions. When the reaction mixture containing **8c** and **9c** was heated in moist

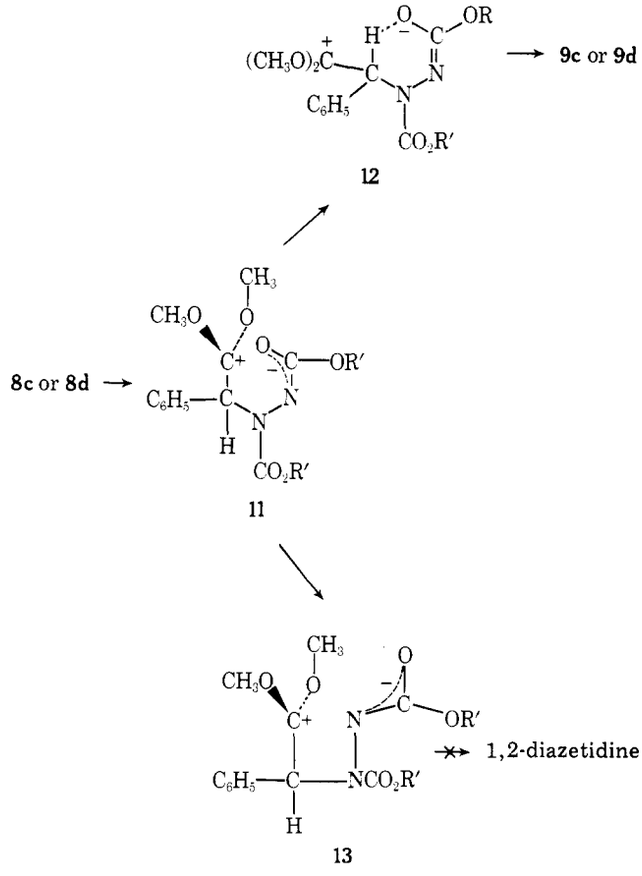
Scheme II



a, R = Cl; R′ = CH_3; R″ = C_2H_5
b, R = Br; R′ = CH_3; R″ = C_2H_5
c, R = C_6H_5; R′ = CH_3; R″ = CH_3
d, R = C_6H_5; R′ = C_2H_5; R″ = CH_3

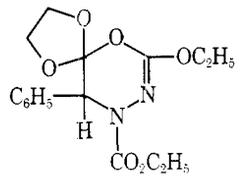
chloroform at 45 °C or when it was subjected to acid catalyzed hydrolysis, both compounds were converted into **10c.**

When diethyl azodicarboxylate and phenylketene dimethyl acetal are mixed at 10 °C in a NMR tube, the 5,6-dihydrooxadiazine **8d** is formed initially as shown by the appearance of the singlet at 5.57 ppm due to the proton at C-5. The peaks of **9d** appear later, indicating that the 5,6-dihydrooxadiazine **8d** is the precursor of the hydrazinylketene acetal **9d.** When the vinyl hydrogen of phenylketene dimethyl acetal is replaced with deuterium and reacted with diethyl azodicarboxylate, the buildup of **9d** can be observed by looking at the N–D peak in the IR spectrum at 2510 cm^{-1}. It seems likely that this reaction involves opening of the 5,6-dihydrooxadiazine to the dipolar structure **11** followed by intramolecular proton transfer to give the hydrazinylketene dimethyl acetal **9.** In principle, the dipolar intermediate **11** could also lead to a 1,2-diazetidine, but this is not observed. Examination of

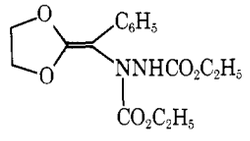


models of the conformation **13** indicates that there is considerable steric interaction between the carboxyl groups. However, the most probable factor determining the product is that the intramolecular proton transfer **11** to **9** is fast.

When 2-phenylmethylene-1,3-dioxolane was reacted with diethyl azodicarboxylate, only the hydrazinylketene acetal **15** was isolated. However, the crude reaction mixture contained a peak at 5.50 ppm (C-5 proton) indicating the presence of the dihydrooxadiazine **14**.

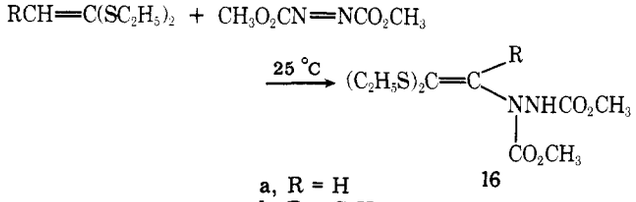


14



15

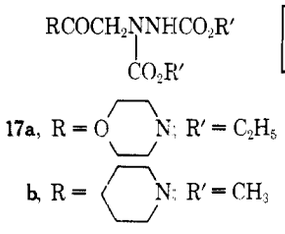
When these reactions were extended to thioacetals, only the hydrazinylketene thioacetals **16a** and **16b** could be isolated. No evidence for the formation of a 5,6-dihydrooxadiazine could be detected. Apparently they are too unstable even at room temperature.



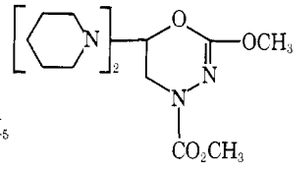
a, R = H
b, R = C_6H_5

16

When 1,1-di(*N*-morpholinyl)ethylene was reacted with diethyl azodicarboxylate, the hydrolysis product **17a** was isolated along with some acetylmorpholine. When 1,1-di(*N*-piperidinyl)ethylene was reacted with dimethyl azodicarboxylate, the hydrolysis product **17b** was isolated along with some acetylpiperidine. In this case, a small amount of the dihydrooxadiazine **18** was also isolated. The elemental analysis of **18** was poor as it was difficult to purify, but the spectral information is consistent. The IR showed no NH, a carbonyl band at 1778 cm^{-1}, and a C=N band at 1620 cm^{-1}. The UV spectrum had maxima at 277 and 308 nm.



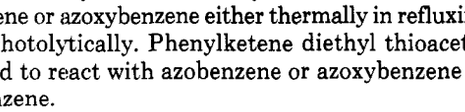
17a, R = morpholino; R′ = C_2H_5
b, R = piperidino; R′ = CH_3



18

Several unsuccessful reactions were attempted. Di(4-chlorophenyl)ketene diethyl acetal failed to react with dimethyl azodicarboxylate even when the benzene solution was refluxed for 19 h. Photolysis of the mixture likewise failed to effect reaction. Phenylketene dimethyl acetal failed to react with azobenzene or azoxybenzene either thermally in refluxing benzene or photolytically. Phenylketene diethyl thioacetal likewise failed to react with azobenzene or azoxybenzene in refluxing benzene.

In each case where 2,2-disubstituted ketene acetals were reacted with azodicarboxylate esters, the reaction either failed because the substituents were electron-withdrawing groups, as in the dibromoketene diethyl acetal or di(4-chlorophenyl)-ketene diethyl acetal cases, or the ene reaction was observed. For example, dimethylketene dimethyl acetal reacted with dimethyl azodicarboxylate to give 2-methyl-3,3-dimethoxy-3-(*N*,*N*′-dicarbomethoxyhydrazinyl)propene-1 (**19**).



19

The data presented give no information as to the mechanism of 5,6-dihydrooxadiazine formation. Firl and Sommer[45] reported that *cis*-1-thioethylpropylene added to dimethyl azodicarboxylate to give 5,6-dihydrooxadiazines in a nonstereospecific manner but gave *cis*-3-methyl-4-ethylthio-1,2-dicarbomethoxy-1,2-dicarbomethoxy-1,2-diazetidine in a stereospecific manner. A dipolar intermediate was postulated in 5,6-dihydrooxadiazine formation, but not in diazetidine formation. It should be pointed out however, that the published information on the three compounds is scanty, and it is not clear how the structural and stereochemical assignments were made.

The observation that **8c** and **8d** were precursors of **9c** and **9d** raises the question as to the thermal stability of 5,6-dihydrooxadiazines in general. Accordingly, 2-methoxy-4-carbomethoxy-6-phenoxy-5,6-dihydrooxadizine, mp 103–104 °C, was prepared as described by Firl and Sommer.[43,44] When heated at 45 °C in deuterated chloroform for 3 weeks, no decomposition could be detected. Apparently, the facile ring opening of the 5,6-dihydrooxadiazines observed in this work is the result of stabilization of the dipole **11** by delocalization of the positive charge by the two alkoxy groups. This may also explain why no 1,2-diazetidines were observed in this work, i.e., if the 5,6-dihydrooxadiazine is unstable, the 1,2-diazetidine should be even less stable relative to the dipolar intermediate.

During the course of this study we noted that reactivity of the alkenes with azodicarboxylate esters followed the order ketene acetals < ketene thioacetals < ketene aminals, i.e., in order of increasing donating power of the alkene. (A similar reactivity was reported for vinyl ethers, vinyl thioethers, and enamines.[41]) This observation provides an explanation as to why 2:1 adducts were observed only in the reactions of ketene dimethyl and diethyl acetals with azodicarboxylate esters. These reactions are slow enough, and the initially formed 5,6-dihydrooxadiazine **1** unstable enough, that the corresponding hydrazinylketene acetal **2** builds up during the reaction, and since it is even a better electron donor than the starting ketene acetal, it reacts with unreacted azocompound to give 2:1 adducts, **4–6**.

Experimental Section

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

Diethyl azodicarboxylate was purchased from Aldrich Chemical Co. and distilled prior to use. Dimethyl azodicarboxylate was prepared by oxidation of the hydrazine by the Rabjohn procedure.[51] Ketene, chloroketene, bromoketene, and dibromoketene diethyl acetals were prepared by the McElvain and Beyerstedt procedure.[52,53] This procedure was also adopted to the preparation of phenylketene dimethyl acetal. Ketene and phenylketene diethyl thioacetals were prepared by the procedure of Rinzema, Stoffelsma, and Arens.[54] 1,1-Di(*N*-piperdinyl)ethylene and 1,1-di(*N*-morpholinyl)ethylene were obtained by the Boganz and Domasche method.[55] Di(4-chlorophenyl)-ketene diethyl acetal was prepared by the method reported by Kaluszyner, Mechoulam, and Cohen.[56,57] Dimethylketene dimethyl acetal was obtained by the McElvain and Davie[58] procedure. The McElvain and Curry method was used to prepare 2-phenylmethylene-1,3-dioxolane.[59]

In order to avoid polymerization of the acetals, all glassware was washed with dilute sodium or potassium hydroxide and water and throughly dried prior to use. The alumina used in the chromatographic separations was neutral, Brockman Activity 1, 80–100 mesh.

Reaction of Ketene Dimethyl Acetal with Dimethyl Azodicarboxylate. Ketene dimethyl acetal (1.602 g, 0.01820 mol) was dissolved in 6 mL of anhydrous benzene and dimethyl azodicarboxylate (2.655 g, 0.01820 mol) in 6 mL of anhydrous benzene was added dropwise. The temperature rose to 42 °C. After standing at room temperature for 2 days, the solvent was removed under vacuum.

A portion of the oily residue (3.934 g) was triturated with anhydrous ether to give 0.893 g of crystalline solid. A second trituration with ether gave 0.387 g (10%) of 2-methoxy-4-carbomethoxy-5-(*N,N'*-dicarbomethoxyhydrazinyl)-6,6-dimethoxy-5,6-dihydrooxadiazine (**4a**): mp 160–162 °C; IR (Nujol) 3320 (NH), 1760, 1750, 1720 (C=O), and 1683 cm^{-1} (C=N); NMR ($CDCl_3$) δ 3.45 (s, 3 H), 3.57 (s, 3 H), and 3.83 (m, 13 H).

Anal. Calcd for $C_{12}H_{20}N_4O_{10}$: C, 37.89; H, 5.30; N, 14.73. Found: C, 37.73; H, 5.20; N, 14.83.

The ether solution from the first trituration was evaporated. The residue (3.041 g) was again triturated with a small volume of ether to give 0.0928 g (3%) of a second solid. Chromatography on alumina, using chloroform as the eluent, followed by recrystallization from petroleum ether–ether (1:1) gave 0.0353 g of pure methyl di(*N,N'*-dicarbomethoxyhydrazinyl)acetate (**6a**): mp 138.5–140 °C; IR (Nujol) 3400 (NH) and 1740 cm^{-1} (C=O); NMR ($CDCl_3$) δ 3.79 (s, 12 H), 3.88 (s, 3 H), 6.15 (s, 1 H), and 7.28 (bs, 1 H).

Anal. Calcd for $C_{11}H_{18}N_4O_{10}$: C, 36.06; H, 4.95; N, 15.29. Found: C, 35.87; H, 5.05; N, 15.04.

Finally, evaporation of the ether soluble material left 2.948 g (73.6%) of a very viscous liquid, which was shown to be methyl *N,N'*-dicarbomethoxyhydrazinylacetate (**3a**) by comparison of its IR and NMR spectra with an authentic sample whose preparation is given below.

***N*-Carbomethoxyhydrazone of Methyl Glyoxylate.** Dimethyl tartrate (5.34 g, 0.0300 mol) was dissolved in 50 mL of glacial acetic acid. The solution was heated at 50 °C while 13.3 g (0.0300 mol) of lead tetraacetate was introduced. Water (200 mL) was then added, followed by a solution of 6.25 g (0.0600 mol) of methyl carbazate in 25 mL of water. After standing at room temperature for 1 week, the solution was extracted with chloroform. The extract was washed twice with sodium bicarbonate (until neutral) and once with water and dried over magnesium sulfate. Evaporation of the chloroform gave 5.70 g (60.9%) of the *N*-carbomethoxyhydrazone of methyl glyoxylate: mp 130.5–131 °C (from chloroform–ether); IR (Nujol) 3190 (NH), 1750, 1733 (C=O), and 1691 cm^{-1} (C=N); NMR ($CDCl_3$) δ 3.80 (s, 6 H) and 7.43 (bs, 1 H).

Anal. Calcd for $C_5H_8N_2O_4$: C, 37.50; H, 5.03; N, 17.49. Found: C, 37.48; H, 5.11; N, 17.44.

Methyl *N'*-Carbomethoxyhydrazinylacetate. The *N*-carbomethoxyhydrazone of methyl glyoxylate (1.304 g, 8.143 mmol) was dissolved in 35 mL of glacial acetic acid. The mixture was hydrogenated over platinum at 35 °C and 35 psi for 24 h. The mixture was diluted with 35 mL of chloroform and extracted five times with 5% hydrochloric acid. The aqueous extracts were neutralized with 10% sodium bicarbonate solution. The basic solution was extracted with chloroform. The extracts were dried over magnesium sulfate and then evaporated to give 0.920 g of oil. Chromatography on alumina, using benzene–chloroform (7:3), gave 0.539 g (58.5%) of pure methyl *N'*-carbomethoxyhydrazinylacetate as a viscous oil: NMR ($CDCl_3$) δ 3.61 (s, 3 H), 3.67 s, 3 H), 3.78 (s, 2 H), 4.46 (bs, 1 H), and 7.34 (bs, 1 H).

Anal. Calcd for $C_5H_{10}N_2O_4$: C, 37.03; H, 6.12; N, 17.27. Found: C, 37.00; H, 6.14; N, 17.10.

Methyl *N,N'*-Dicarbomethoxyhydrazinylacetate (3a). Methyl *N'*-carbomethoxyhydrazinylacetate (0.643 g, 4.08 mmol) was dissolved in 8 mL of methanol and 2 mL of water. The solution was cooled in an ice bath and 0.380 g (4.10 mmol) of methyl chloroformate and a solution of 0.211 g (1.98 mmol) of sodium carbonate in 3 mL of water were added. The temperature was kept below 15 °C. After the additions were complete, the reaction was stirred at room temperature for 30 min. It was extracted with chloroform. The extracts were dried over magnesium sulfate. Evaporation of the solvent gave 0.752 g of crude product. Chromatography on alumina using chloroform–ether (2:1) as eluent gave 0.470 g (52.3%) of methyl *N,N'*-dicarbomethoxyhydrazinylacetate (**3a**) as a viscous oil: IR (neat) 3280 (NH), 1748, and 1716 cm^{-1} (C=O); NMR ($CDCl_3$) δ 3.72 (s, 6 H), 4.28 (s, 3 H), and 7.14 (bs, 1 H).

Anal. Calcd for $C_7H_{12}N_2O_6$: C, 38.18; H, 5.49; N, 12.72. Found: C, 38.25; H, 5.54; N, 12.69.

Reaction of Ketene Dimethyl Acetal with Diethyl Azodicarboxylate. In 6 mL of anhydrous benzene was dissolved 2.400 g (0.02726 mol) of ketene dimethyl acetal and 4.750 g (0.02726 mol) of diethyl azodicarboxylate was added dropwise. The temperature rose to 48 °C, After standing a short time at room temperature, the benzene was removed under vacuum.

A portion of the residue (0.545 g) was separated by preparative TLC on silica gel (MCB, SX144-5, 60–200 mesh). Pentane–ether (1:2) was the eluent. Separation gave 0.282 g (51.8%) of methyl *N,N'*-dicarboethoxyhydrazinylacetate (**3b**). Recrystallization from ether gave pure material: mp 73–74.5 °C; IR (Nujol) 3250 (NH), 1745, and 1720 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.29 (t, 6 H), 3.72 (s, 3 H), 4.25 (q, 4 H), 4.34 (s, 2 H), 7.01 (bs, 1 H). This compound was identical (IR, NMR, mixture melting point) to the authentic sample prepared below.

Anal. Calcd for $C_9H_{16}N_2O_6$: C, 43.59; H, 6.49; N, 11.28. Found: C, 43.42; H, 6.43; N, 11.20.

The NMR spectrum of the reaction mixture indicated the presence of two additional compounds. These are methyl di(*N,N'*-dicarboethoxyhydrazinyl)acetate (**6b**) (NMR ($CDCl_3$) δ 3.25 (s, 6 H) and 7.38 (bs, 1 H)) and 1,1-dimethoxy-2,2-di(*N,N'*-dicarboethoxyhydrazinyl)ethylene (**5b**) (NMR ($CDCl_3$) δ 3.78 (s, 3 H), 6.04 (s, 1 H), and 7.35 (bs, 1 H)). These assignments are consistent with those of the compounds isolated in the reaction of ketene dimethyl acetal with dimethyl azodicarboxylate. From the NMR of the reaction mixture it is estimated that the ratio of **3b:6b:5b** is 40%:28%:32%.

***N*-Carboethoxyhydrazone of Methyl Glyoxylate.** The same procedure given above for the carbomethoxy compound gave a 35% yield of the hydrazone: mp 129–130 °C (lit.[60] mp 130 °C); NMR ($CDCl_3$) δ 1.3 (t, 3 H), 3.77 (s, 3 H), 4.23 (q, 2 H), and 7.41 (s, 1 H).

Methyl *N'*-Carboethoxyhydrazinylacetate. The same procedure was used as for the corresponding carbomethoxy compound given above except the hydrogenation time was 48 h. Workup gave a 31.7% yield: mp 53–54 °C; NMR ($CDCl_3$) δ 1.23 (t, 3 H), 3.66 (s, 3 H), 3.70 (s, 3 H), 4.10 (q, 2 H), and 7.31 (bs, 1 H).

Anal. Calcd for $C_6H_{12}N_2O_4$: C, 40.90; H, 6.89; N, 15.90. Found: C, 40.92; H, 6.91; N, 15.86.

Methyl *N,N'*-Dicarboethoxyhydrazinylacetate (3b). The reaction was run in the same way as with the corresponding carbomethoxy compound above. Evaporation of the chloroform extract gave 1.52 g (from 1.20 g, 6.83 mmol of the starting compound) of viscous oil, which solidified on standing. Recrystallization from ether gave 1.32 g (78%) of methyl *N,N'*-dicarboethoxyhydrazinylacetate (**3b**): mp 73–74 °C; IR (Nujol) 3250 (NH), 1745, and 1720 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.29 (t, 6 H), 3.79 (s, 3 H), 4.25 (q, 4 H), 4.34 (s, 2 H), 7.01 (bs, 1 H).

Reaction of Ketene Diethyl Acetal with Dimethyl Azodicarboxylate. In 3 mL of anhydrous benzene was dissolved 1.329 g (0.01145 mol) of ketene diethyl acetal and 1.993 g (0.01145 mol) of dimethyl azodicarboxylate in 3 mL of anhydrous benzene added dropwise. The temperature rose to 48 °C. After standing at room temperature for 2 days, the solvent was removed and the residue was triturated with anhydrous ether to give 1.712 g (62.1%) of ethyl di(*N,N'*-dicarbomethoxyhydrazinyl)acetate (**6c**). Recrystallization from toluene gave pure material: mp 117–118.5 °C; IR (Nujol) 3335 (NH) and 1740 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.30 (t, 3 H), 3.7 (s, 12 H), 4.25 (q, 2 H), 6.05 (s, 1 H), and 7.04 (bs, 2 H).

Anal. Calcd for $C_{12}H_{20}N_4O_{10}$: C, 37.89; H, 5.30; N, 14.73. Found: C, 37.90; H, 5.41; N, 14.73.

Reaction of Ketene Diethyl Acetal with Diethyl Azodicarboxylate. Diethyl azodicarboxylate (5.97 g, 0.0343 mol) was added dropwise to ketene diethyl acetal (3.98 mol). The temperature rose to 68 °C. On long standing, the very viscous mixture solidified. Recrystallization from petroleum ether containing a few drops of ether gave 5.43 g (73.3%) of ethyl di(*N,N'*-dicarboethoxyhydrazinyl)acetate (**6d**): IR (Nujol) 3300 (NH), 1750, and 1725 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.27 (t, 6 H), 1.30 (t, 3 H), 4.15 (q, 10 H), 5.02 (s, 1 H), and 7.09 (bs, 2 H).

Anal. Calcd for $C_{16}H_{28}N_4O_{10}$: C, 44.03; H, 6.46; N, 12.83. Found: C, 43.88; H, 6.51; N, 12.81.

Reaction of Chloroketene Diethyl Acetal with Dimethyl Azodicarboxylate. Chloroketene diethyl acetal (1.870 g, 0.01253 mol) was dissolved in 10 mL of anhydrous benzene and dimethyl azodicarboxylate (1.815 g, 0.01243 mol) in 5 mL of anhydrous benzene was added dropwise. The temperature rose to 29 °C. After standing at room temperature for 3 days, the benzene was removed under vacuum. A portion of the residue (0.4206 g) was separated on a silica gel column (MCB SX1144-5, 60–200 mesh) using benzene–ether (3:1) as eluent. The main fraction, 0.209 g (49.7%), was a viscous oil (a glass) with the following spectral characteristics: IR (neat) 3300 (NH), 1750, and 1730 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.18 (t, 6 H), 3.60 (s, 3 H), 3.67 (s, 2 H), 4.10 (q, 6 H), 6.43 (s, 1 H), and 6.95 (bs, 1 H). These spectral data indicate that the compound is primarily ethyl *N,N'*-dicarbomethoxy-2-chlorohydrazinylacetate (**10a**).

Reaction of Bromoketene Diethyl Acetal with Dimethyl Azodicarboxylate. Dimethyl azodicarboxylate (1.552 g, 0.01063 mol)

was dissolved in 6 mL of anhydrous benzene and added dropwise to a solution of bromoketene diethyl acetal (2.071 g, 0.01063 mol) in 10 mL of anhydrous benzene. The temperature rose to 30 °C. The reaction mixture was allowed to stand at room temperature for 2 days. A portion (0.450 g) of the residue, after removal of the benzene, was placed on a silica gel column (MCB SX1144-5, 60–200 mesh). Elution with benzene–ether (3:1) gave 0.1573 g (35.1%) of a viscous oil with the following spectral characteristics: IR (neat) 3300 (NH) and 1770 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.31 (t, 6 H), 3.73 (s, 3 H), 3.80 (s, 3 H), 4.23 (q, 4 H), 6.73 (s, 1 H), and 6.85 (bs, 1 H). Since this glasslike material could not be purified, no elemental analysis was obtained. However, the spectral information is consistent with **10b.**

Reaction of Phenylketene Dimethyl Acetal with Dimethyl Azodicarboxylate. In 4 mL of dry benzene was dissolved 2.208 g (0.01512 mol) of dimethyl azodicarboxylate and 2.479 g (0.01512 mol) of phenylketene dimethyl acetal in 10 mL of dry benzene added dropwise. The temperature rose to 33 °C. After standing for 4 days, the precipitate which formed was filtered and recrystallized from toluene with a yield of 1.994 g (42.5%) of 1,1-dimethoxy-2-phenyl-2-(*N,N'*-dicarbomethoxyhydrazinyl)ethylene (**9c**): mp 138.5–140 °C; IR (Nujol) 3220 (NH), 1750, 1700 (C=O), and 1695 cm^{-1} (C=C); NMR ($CDCl_3$) δ 3.59 (s, 3 H), 3.63 (s, 3 H), 3.65 (s, 6 H), 6.95 (bs, 1 H), and 7.08–7.65 (m, 5 H).

Anal. Calcd for $C_{14}H_{18}N_2O_6$: C, 54.18; H, 5.84; N, 9.02. Found: C, 54.19; H, 5.85; N, 8.93.

The NMR of the original mixure before separation revealed the presence of two compounds, the isolated hydrazinylethylene **9c** (66.3%) and 2,6,6-trimethoxy-4-carbomethoxy-5-phenyl-5,6-dihydrooxadiazine (**8c**) (33.7%): NMR ($CDCl_3$) δ 3.27 (t, 3 H), 3.34 (s, 3 H), 3.7 (s, 3 H), 3.81 (s, 3 H), 5.55 (s, 1 H), and 7.08–7.25 (m, 5 H).

A portion of the oily residue remaining after separation of the hydrazinylethylene **9c,** which was enriched with the dihydrooxadiazine, was heated in wet deuteriochloroform for 30 min at 45 °C. The NMR peaks of the dihydrooxadiazine disappeared as it was transformed into methyl *N,N'*-dicarbomethoxy-2-phenylhydrazinylacetate (**10c**).

In an unsuccessful attempt to isolate the dihydrooxadiazine, a portion (0.3478 g) of the residue after separation of the bulk of the 1,1-dimethoxy-2-phenyl-2-(*N,N'*-dicarbomethoxyhydrazinyl)-ethylene (**9c**) was chromatographed on silica gel (MCB 5 × 1144-5, 60–200 mesh). Elution with chloroform–ether (3:1) gave 0.1425 g (41%) of the hydrolysis product, methyl *N,N'*-dicarbomethoxy-2-phenylhydrazinylacetate (**10c**), as a viscous oil. On trituration with ether it solidified. Recrystallization from petroleum ether containing a few drops of ether gave pure material: mp 111–112.5 °C; IR (Nujol) 3300 (NH) and 1725 cm^{-1} (C=O); NMR ($CDCl_3$) δ 3.72 (s, 3 H), 3.75 (s, 6 H), 5.95 (s, 1 H), 6.77 (bs, 1 H), and 7.23 (s, 5 H).

Anal. Calcd for $C_{13}H_{16}N_2O_6$: C, 52.70; H, 5.44; N, 9.45. Found: C, 52.72; H, 5.26; N, 9.29.

When 0.14 g of 1,1-dimethoxy-2-phenyl-2-(*N,N'*-dicarbomethoxyhydrazinyl)ethylene was heated in wet chloroform at 45 °C for 98 h, it was hydrolyzed quantitatively to methyl *N,N'*-dicarbomethoxy-2-phenylhydrazinylacetate (**10c**), mp 110–112.5 °C; mixture melting point gave no depression.

Reaction of Phenylketene Dimethyl Acetal with Diethyl Azodicarboxylate. In 5 mL of dry benzene was dissolved 2.475 g (0.01423 mol) of dimethyl azodicarboxylate which was added dropwise to a solution of 2.333 g (0.01423 mol) in 5 mL of dry benzene. The temperature rose to 27 °C. The reaction mixture was allowed to stand at room temperature for 6 days. The precipitated 1,1-dimethoxy-2-phenyl-2-(*N,N'*-dicarboethoxyhydrazinyl)ethylene (**9d**) was filtered to give 4.138 g (85.9%): mp 115–116 °C; IR (Nujol) 3270 (NH), 1750, 1700 (C=O), and 1690 cm^{-1} (C=C); NMR ($CDCl_3$) δ 1.21 (t, 6 H), 3.58 (s, 3 H), 3.67 (s, 3 H), 4.11 (q, 4 H), 6.83 (bs, 1 H), and 7.08–7.70 (m, 5 H).

Anal. Calcd for $C_{16}H_{22}N_2O_6$: C, 56.79; H, 6.55; N, 8.27. Found: C, 56.76; H, 6.62; N, 8.32.

Recrystallization of this hydrazinylethylene from moist toluene gave a quantitative yield of methyl *N,N'*-dicarboethoxy-2-phenylhydrazinylacetate (**10d**): mp 91.5–92.5 °C: IR (Nujol) 3285 (NH), 1733, and 1675 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.30 (t, 6 H), 3.77 (s, 3 H), 4.23 (q, 4 H), 6.03 (s, 1 H), 6.76 (bs, 1 H), and 7.30 (s, 5 H).

Anal. Calcd for $C_{15}H_{20}N_2O_6$: C, 55.54; H, 6.21; N, 8.63. Found: C, 55.53; H, 6.33; N, 8.50.

The NMR spectrum of the reaction mixture, before separation of the hydrazinylethylene, indicated the presence of two compounds, the hydrazinylethylene **9d** (83.4%) and 2-ethoxy-4-carboethoxy-5-phenyl-6,6-dimethoxy-5,6-dihydrooxadiazine (**8d**) (16.6%): partial NMR ($CDCl_3$) δ 3.28 (s, 3 H), 3.36 (s, 3 H), 4.09 (q, 4 H), 5.57 (s, 1 H).

When the above reaction was repeated, using acetonitrile as the solvent instead of benzene, a 50% yield of the hydrazinylethylene **9d** was isolated.

Reaction of 2-Phenylmethylene-1,3-dioxolane with Diethyl Azodicarboxylate. In 10 mL of dry benzene was placed 2.684 g (0.01660 mol) of 2-phenylmethylene-1,3-dioxolane and to this solution was added dropwise 2.888 g (0.01660 mol) of diethyl azodicarboxylate in 5 mL of dry benzene. After standing at room temperature for 2 days, the benzene was removed under vacuum. The oily residue was chromatographed on alumina. Elution with benzene gave 2.33 g (41.8%) of 2-[phenyl(*N,N'*-dicarboethoxyhydrazinyl)methylene]-1,3-dioxolane (**15**): mp 138–139.5 °C; IR (Nujol) 3300 (NH), 1750, 1710 (C=O), and 1665 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.23 (t, 6 H), 4.16 (q, 4 H), 4.35 (m, 4 H), 6.97–7.75 (m, 6 H).

Anal. Calcd for $C_{16}H_{20}N_2O_6$: C, 57.13; H, 5.99; N, 8.32. Found: C, 57.36; H, 6.02; N, 8.36.

The NMR spectrum of the crude reaction mixture showed a singlet at 4.40 ppm, suggesting the presence of a 5,6-dihydrooxadiazine, but this compound could not be isolated.

Reaction of Ketene Diethyl Thioacetal with Dimethyl Azodicarboxylate. Dimethyl azodicarboxylate (1.269 g, 8.690 mmol) was dissolved in 5 mL of anhydrous benzene and added dropwise to a solution of ketene diethyl thioacetal (1.276 g, 8.690 mmol) in 5 mL of dry benzene. The temperature rose to 37 °C. After standing at room temperature for 3 days, the solvent was evaporated. A portion (0.6221 g) of the residue was chromatographed on alumina. Elution with chloroform gave 0.3481 g (55.9%) of pure 1,1-diethylthio-2-(*N,N'*-dicarbomethoxyhydrazinyl)ethylene (**16a**) as an oil: IR (neat) 3210 (NH), 1725, 1700 (C=O), and 1650 cm^{-1} (C=C); NMR ($CDCl_3$) δ 1.18 (t, 3 H), 1.21 (t, 3 H), 2.67 (q, 2 H), 2.78 (q, 2 H), 3.71 (s, 3 H), 3.78 (s, 3 H), 7.17 (s, 1 H), 7.53 (bs, 1 H).

Anal. Calcd for $C_{10}H_{18}N_2O_4S_2$: C, 40.80; H, 6.16; S, 21.73. Found: C, 40.66; H, 5.98; S, 21.94.

Reaction of Phenylketene Diethyl Thioacetal with Dimethyl Azodicarboxylate. Dimethyl azodicarboxylate (1.317 g, 9.020 mmol) was dissolved in 5 mL of anhydrous benzene and added dropwise to a solution of phenylketene diethyl thioacetal (2.021 g, 9.202 mmol) in 10 mL of dry benzene. After standing 2 days at room temperature, the solvent was removed and a portion (0.553 g) of the residue was chromatographed on alumina. Elution with benzene–chloroform (1:1) gave 0.498 g (90.1%) of 1,1-diethylthio-2-phenyl-2-(*N,N'*-dicarbomethoxyhydrazinyl)ethylene (**16b**) as a viscous oil: IR (neat) 3290 (NH) and 1725 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.11 (t, 3 H), 1.28 (t, 3 H), 2.62 (q, 2 H), 2.87 (q, 2 H), 3.6 (s, 3 H), 3.7 (s, 3 H), 6.91 (bs, 1 H), 7.17–7.50 (m, 5 H).

Anal. Calcd for $C_{16}H_{22}N_2O_4S_2$: C, 5187; H, 5.98; N, 7.56; S, 17.30. Found: C, 51.47; H, 6.02; N, 7.47; S, 17.51.

Reaction of 1,1-Di(*N*-piperidinyl)ethylene with Dimethyl Azodicarboxylate. Dimethyl azodicarboxylate (1.746 g, 0.01145 mol) in 5 mL of anhydrous benzene was added dropwise to a solution of 1,1-di(*N*-piperidinyl)ethylene (2.415 g, 0.01195 mol) in 10 mL of dry benzene. The temperature rose to 43 °C. After standing 3 days, the benzene was removed and a portion (1.751 g) of the crude reaction mixture was chromatographed on alumina. Elution with benzene gave 0.1647 g (9.4%) of acetylpiperidine. Elution with chloroform gave 0.1080 g (6.2%) of 2-methoxy-4-carbomethoxy-6,6-di(*N*-piperidinyl)-5,6-dihydrooxadiazine (**18**): mp 161–162.5 °C (from chloroform–ether, 1:1); IR (Nujol) 1778 (C=O) and 1620 cm^{-1} (C=N); NMR ($CDCl_3$) δ 1.72 (b, 12 H), 3.46 (b, 8 H), 3.60 (s, 3 H), 3.72 (s, 3 H), and 3.75 (s, 2 H); UV ($CHCl_3$) λ 277 (E 4.92 × 10^4) 308 nm (E 5.67 × 10^4).

Anal. Calcd for $C_{16}H_{28}N_4O_4$: C, 56.48; H, 8.20; N, 18.98. Found: C, 55.65; H, 7.70; N, 18.98.

Further elution with chloroform gave 0.7115 g (40.6%) of *N,N'*-dicarbomethoxyhydrazinylacetylpiperidine (**17b**): mp 159–160 °C (from chloroform–ether 1:1); IR (Nujol) 3180 (NH), 1725, and 1710 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.60 (b, 6 H), 3.27–3.48 (b, 4 H), 3.70 (s, 6 H), 4.30 (s, 2 H), 7.20 (s, 1 H).

Anal. Calcd for $C_{11}H_{19}N_3O_5$: C, 48.43; H, 7.00; N, 15.37. Found: C, 48.13; H, 7.05; N, 15.04.

Reaction of 1,1-Di(*N*-morpholinyl)ethylene with Diethyl Azodicarboxylate. Diethyl azodicarboxylate (2.202 g, 0.01266 mol) was dissolved in 5 mL of dry benzene and this solution was added dropwise to 2.507 g (0.01266 mol) of 1,1-di(*N*-morpholinyl)ethylene in 10 mL of dry benzene. The temperature rose to 47 °C. After standing at room temperature for 3 days, the benzene was removed and a portion (1.745 g) of the residue was chromatographed on alumina. Elution with chloroform gave 1.054 g of an oil. A portion (0.6904 g) of this oil was rechromatographed. Elution with benzene–chloroform (4:1) gave 0.2144 g (31.1%) of acetylmorpholine. Elution with

benzene–chloroform (2:1) gave 0.2455 g (17.6%) of *N,N'*-dicarboethoxyhydrazinylacetylmorpholine (**17a**): mp 124–125 °C; IR (Nujol) 3340 (NH), 1750, 1730, and 1662 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.30 (t, 6 H), 3.63 (b, 8 H), 4.20 (g, 4 H), 4.36 (s, 2 H), 7.21 (b, 1 H).

Anal. Calcd for $C_{12}H_{21}N_3O_6$: C, 47.51; H, 6.97; N, 13.85. Found: C, 47.80; H, 7.20; N, 13.71.

Reaction of Dimethylketene Dimethyl Acetal with Dimethyl Azodicarboxylate. Dimethyl azodicarboxylate (2.292 g, 0.01570 mol) was dissolved in 10 mL of anhydrous benzene and added dropwise to a solution of dimethylketene dimethyl acetal (1.821 g, 0.01570 mol) in 10 mL of dry benzene. After standing at room temperature for 1 day, the solvent was removed under vacuum. The resulting oil was triturated with carbon tetrachloride and the resulting precipitate filtered. Recrystallization from petroleum ether–ether (2:1) gave 2.8 g (68.2%) of 2-methyl-3,3-dimethoxy-3-(*N,N'*-dicarbomethoxyhydrazinyl)propene-1 (**19**): mp 101–102 °C; IR (Nujol) 3320 (NH), 1765, 1710 (C=O), and 1565 cm^{-1} (C=C); NMR ($CDCl_3$) δ 1.72 (s, 3 H), 3.13 (s, 3 H), 3.27 (s, 3 H), 3.70 (s, 6 H), 5.31 (s, 1 H), 5.40 (s, 1 H), 6.82 (bs, 1 H).

Anal. Calcd for $C_{10}H_{18}N_2O_6$: C, 45.79; H, 6.91; N, 10.68. Found: C, 45.99; H, 6.95; N, 10.65.

Deuterated Benzyl Cyanide. Freshly distilled benzyl cyanide (20 g, 0.1702 mol) was dissolved in 68 mL of anhydrous benzene, and a solution of sodium deuterioxide, prepared from 3.57 g (0.155 g-atom) of sodium and 68 g (3.4 mol) of heavy water, was added along with 1.95 g of Aliquat 336. The reaction mixture was stirred 40 min at room temperature and then was neutralized with ammonium chloride solution in heavy water. The benzene layer was separated and dried over anhydrous magnesium sulfate. The deuterated benzyl cyanide was distilled under reduced pressure, bp 106–107.5 °C (12 mm). The NMR (CCl_4) showed only the peak at 7.25 ppm for the aromatic hydrogens.

Deuterated Methyl Phenyliminoacetate Hydrochloride. Deuterated benzyl cyanide (17.8 g, 0.1495 mol) was dissolved in 5.25 g (0.1641 mol) of anhydrous methanol and the solution cooled in an ice bath. A stream of hydrogen chloride was bubbled through the mixture until 5.5 g had been absorbed. Anhydrous ether (56 mL) was added and the mixture refrigerated overnight. The product was filtered and washed with anhydrous ether until neutral and then dried in a desiccator over sodium hydroxide: yield 21.3 g (76%); IR (Nujol) 3320 (NH) and 1635 cm^{-1} (C=N); NMR ($CDCl_3$) δ 4.27 (s, 3 H) and 7.40 (s, 5 H).

Deuterated Methyl Orthophenylacetate. Deuterated phenyliminoacetate hydrochloride (21.3 g, 0.1511 mol) was dissolved in 25 mL of absolute methanol and the mixture allowed to stand 2 days at room temperature. Anhydrous ether (13 mL) was added and the ammonium chloride which precipitated was filtered. The solvent was evaporated from the filtrate and the residue was distilled from sodium hydride: yield 8.9 g (22.5%); bp 118–119 °C (5 mm) (lit.[61] bp 73–76 °C (0.4 mm)); NMR (CCl_4) δ 3.16 (s, 6 H) and 7.17 (s, 5 H).

Deuterated Phenylketene Dimethyl Acetal. Deuterated methyl orthophenylacetate (8.90 g, 0.0449 mol) was mixed with 5.40 g (0.0450 mol) of anhydrous aluminum methoxide and the mixture heated in an oil bath at 210 °C. When the evolution of alcohol ceased, the pressure was lowered and the residue fractionated through a 30 cm vacuum jacketed column: yield, 2.2 g (28.3%); bp 72–73 °C (0.9 mm); IR (neat) 1640 cm^{-1}; NMR ($CDCl_3$) δ 3.62 (s, 3 H), 3.72 (s, 3 H), and 3.26 (s, unreacted orthoester). The material obtained contained about 19% unreacted methyl orthophenylacetate.

Registry No.—**3a,** 66769-46-8; **3b,** 66750-48-9; **4a,** 66750-49-0; **5b,** 66750-50-3; **6a,** 66750-51-4; **6b,** 66750-52-5; **6c,** 66750-53-6; **6d,** 66750-54-7; **8c,** 66750-55-8; **8d,** 66750-56-9; **9c,** 66750-57-0; **9d,** 66750-58-1; **10a,** 66750-59-2; **10b,** 66750-60-5; **10c,** 66750-61-6; **10d,** 66750-33-2; **15,** 66750-34-3; **16a,** 66750-35-4; **16b,** 66750-36-5; **17a,** 66750-37-6; **17b,** 66750-38-7; **18,** 66750-39-8; **19,** 66750-40-1; ketene dimethyl acetal, 922-69-0; dimethyl azodicarboxylate, 2446-84-6; methyl glyoxylate *N*-carbomethoxyhydrazone, 66750-41-2; dimethyl tartrate, 608-68-4; methyl carbazate, 6294-89-9; methyl *N'*-carbomethoxyhydrazinylacetate, 66750-42-3; diethyl azodicarboxylate, 1972-28-7; methyl glyoxyate *N*-carboethoxyhydrazone, 5576-74-9; diethyl tartrate, 87-91-2; methyl *N'*-carboethoxyhydrazinylacetate, 66750-43-4; ketene diethyl acetal, 2678-54-8; chloroketene diethyl acetal, 42520-09-2; bromoketene diethyl acetal, 42520-11-6; phenylketene dimethyl acetal, 13049-41-7; 2-phenylmethylene-1,3-dioxolane, 4362-17-8; ketene diethyl thioacetal, 4992-59-0; phenylketene diethyl thioacetal, 66750-44-5; 1,1-di(*N*-piperidinyl)ethylene, 42259-31-4; *N*-acetyl piperidine, 618-42-8; 1,1-di(*N*-morpholinyl)-ethylene, 14212-87-4; *N*-acetylmorpholine, 1696-20-4; dimethylketene dimethyl acetal, 5634-54-8; benzyl-α,d_2 cyanide, 935-66-0; benzyl cyanide, 140-29-4; $PhCD_2C(NH)OMe \cdot HCl$, 66750-45-6; $PhCD_2C(OH)_2OMe$, 66750-46-7; phenylketene-2-*d*-dimethyl acetal, 66750-47-8.

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