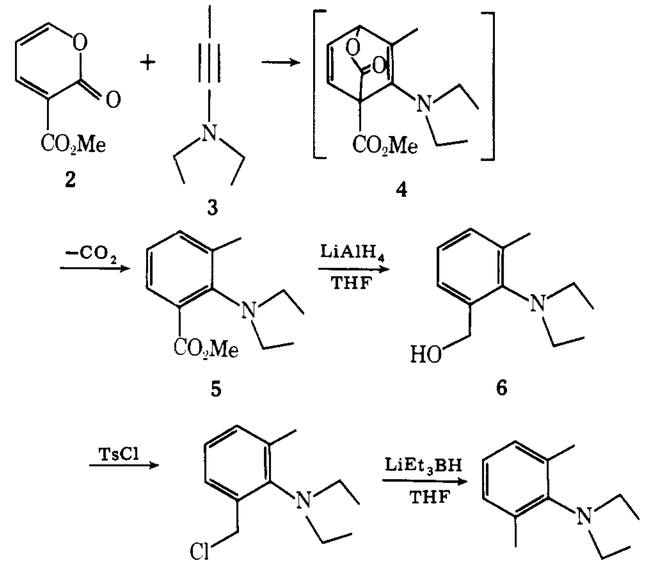
Scheme II



dition reactions,[2] but it has proved to be a poor Diels–Alder reagent. However, diene 2, derived from 1,[3] readily undergoes cycloaddition (Diels–Alder) reactions as demonstrated previously by Corey[4] and others as illustrated in Scheme I.

When ynamine 3 is added to a benzene solution of 2, an exothermic reaction occurs affording adduct 5 (Scheme II). The initial assumption as to the favored orientation of the diene (2) and dienophile (3), based on the polarization of these reagents, proved to be correct. The reaction proceeds in a unidirectional cycloaddition process, presumably through an adduct such as 4, that spontaneously loses CO_2 resulting in formation of 5. Amino ester 5 exhibits the physical and spectral properties expected for an aromatic amine with hindered rotation about the nitrogen–aromatic ring carbon bond.

Reduction of ester 5 affords a second unsymmetrical hindered amine 6 which is further transformed to chloride 7 on treatment with *p*-toluenesulfonyl chloride. Although it is not unusual to form chlorides from the reaction of an alcohol with tosyl chloride, it is suspected that the severe crowding present in the tosylate 6 probably accelerates the formation of chloride 7. Symmetrical diethylamino-*o*-xylene 8 is readily available from lithium triethylborohydride ($LiEt_3BH$/THF) reduction of 7. As in the case for amines 5 and 6, the steric crowding about the *N*,*N*-diethylamino group in 7 and 8 seems to preclude any effective overlap of the nitrogen lone pair with the aromatic ring. Clearly alterations in the ynamine to be added to butadiene 2 would conveniently provide other hindered amines in this series that are of some theoretical interest.

Experimental Section

Methyl 2-(*N*,*N*-Diethylamino)-3-methylbenzoate (5). 1-Diethylamino-1-propyne (3, 1.08 g, 9.73 mmol) was added to α-pyrone 2[6] (1.49 g, 9.73 mmol) in dry benzene (35 mL at room temperature). After addition the reaction mixture was stirred and heated under reflux overnight, cooled, poured into CH_2Cl_2 (50 mL), washed with H_2O (50 mL), and dried ($MgSO_4$). The solvent was removed at reduced pressure and distillation (Kugelrohr oven, 80–90 °C, 0.5 mmHg) afforded 1.70 g (79%) of substituted 5: ^1H NMR δ_{CDCl_3} (Me_4Si) 7.43–6.90 (m, 3 H, PhH), 3.88 (s, 3 H, $-OCH_3$), 3.07 (q, J = 7 Hz, 4 H, $-CH_2-$), 2.31 (s, 3 H, $PhCH_3$), 1.02 (t, J = 7 Hz, 6 H, $-CH_3$); ^{13}C NMR (relative to Me_4Si, $CDCl_3$) 169.89 (carbonyl), 148.58, 138.70, 132.11 (fully substituted aromatic carbons), 133.63, 127.23, 123.93 (aromatic methynes), 51.96 ($-OCH_3$), 47.53 (R_2NCH_2-), 19.26 ($PhCH_3$), 14.68 ppm ($-CH_3$'s); IR (film) 1735, 1650, 1590 cm^{-1}; λ_{max} (EtOH) 235 nm; *m/e* 221. Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65. Found: C, 70.63; H, 8.59.

***N*,*N*-Diethyl-2-hydroxymethyl-6-methylaniline (6).** Aminomethyl benzoate 5 (0.5 g, 2.26 mmol) in THF (10 mL) was added to lithium aluminum hydride (0.08 g, 2.26 mmol) in THF (20 mL) at 0 °C. The suspension was stirred at room temperature (1 h) and excess hydride was quenched with 10% NaOH. The reaction mixture was filtered and the aluminum salts were washed with cold THF (25 mL) and H_2O (25 mL). The filtrate was dissolved in CH_2Cl_2 (75 mL), washed with H_2O (50 mL) and saturated NaCl (75 mL), and dried ($MgSO_4$). The solvent was removed at reduced pressure and the reaction mixture was distilled (Kugelrohr oven, 90–100 °C, 0.5 mmHg) affording 0.30 g (71%) of amino alcohol 6: ^1H NMR δ_{CDCl_3} (Me_4Si) 7.01 (s, 3 H, PhH), 5.06 (s, broad, 1 H, $-OH$), 4.75 (s, 2 H, $-CH_2-$), 3.10 (q, J = 7 Hz, 4 H, $-CH_2-$), 2.29 (s, 3 H, $-CH_3$), 1.04 (t, J = 7 Hz, 6 H, $-CH_3$); IR (film) 3380 cm^{-1}; *m/e* 193.

***N*,*N*-Diethyl-2-chloromethyl-6-methylaniline (7).** Tosyl chloride (1.48 g, 7.77 mmol) in CH_2Cl_2 (15 mL) was added at room temperature to amino alcohol 6 (1.50 g, 7.77 mmol) and triethylamine (0.78 g, 7.77 mmol) in CH_2Cl_2 (75 mL). After stirring for 12 h, the reaction mixture was diluted with CH_2Cl_2 (75 mL), washed with H_2O (100 mL) and saturated aqueous NaCl (100 mL), and dried ($MgSO_4$). The solvent was removed at reduced pressure and distilled (Kugelrohr oven, 60–70 °C, 0.5 mmHg) yielding 1.20 g (73%) of amino chloride 7: ^1H NMR δ_{CDCl_3} (Me_4Si) 7.38–6.97 (m, 3 H, PhH), 4.77 (s, 2 H, $-CH_2Cl$), 3.08 (q, J = 8 Hz, 4 H, $-CH_2-$), 2.25 (s, 3 H, $PhCH_3$), 1.01 (t, J = 8 Hz, 6 H, $-CH_3$); IR (film) 1590 cm^{-1}; *m/e* 211.

***N*,*N*-Diethyl-2,6-dimethylaniline[5] (8).** Lithium triethylborohydride (2.38 mmol, 1 M in THF) was added to amino chloride (0.25 g, 1.18 mmol) in THF (20 mL) at 0 °C. The reaction mixture was allowed to equilibrate to room temperature and stirred for 2 h. Excess hydride was destroyed by the addition of H_2O, and the organoborane intermediates were oxidized by stirring at room temperature overnight with 10% NaOH (10 mL) and H_2O_2 (30%, 10 mL). The reaction mixture was poured into $CHCl_3$ (25 mL) and extracted with $CHCl_3$ (3 × 25 mL). The organic extracts were washed with H_2O (50 mL) and saturated NaCl (50 mL) and dried ($MgSO_4$). The solvent was removed at room temperature and distillation (Kugelrohr oven, 50–75 °C, 0.5 mmHg) afforded 0.17 g (81%) of the desired substituted aniline 8: ^1H NMR δ_{CDCl_3} (Me_4Si) 6.95 (s, 3 H, PhH), 3.07 (q, J = 8 Hz, 4 H, $-CH_2-$), 2.27 (s, 6 H, $PhCH_3$), 0.99 (t, J = 8 Hz, 6 H, $-CH_3$); ^{13}C NMR (relative to Me_4Si, $CDCl_3$) 138.30, 128.8, 128.62, 124.84 (aromatic carbons), 47.37 (R_2NCH_2), 19.54 ($PhCH_3$), 14.77 ppm ($-CH_3$); IR (film) 1590 cm^{-1}; *m/e* 177.

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Registry No.—**2**, 25991-27-9; **3**, 4231-35-0; **5**, 41895-85-6; **6**, 62601-02-9; **7**, 62601-03-0; **8**, 3995-38-8.

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(6) Reference 3 describes the preparation of ethyl α-pyrone-3-carboxylate which was followed for the preparation of the methyl ester **2**.

Intramolecular Decomposition of Isopropylidene Diazomalonate (Diazo Meldrum's Acid)[1c]

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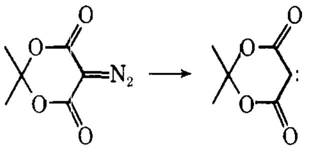
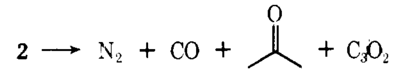
In a discussion of the nonstereospecific addition to olefins of the carbene 1 derived from Meldrum's acid via the diazo compound 2, it was noted that direct irradiation of 2 led, in addition to 1–2% of addition products, to "very little product of any kind".[2] We report here on the fate of 1 generated by pyrolysis and photolysis of 2.

Pyrolysis of 2 at 320 °C was carried out under vacuum in



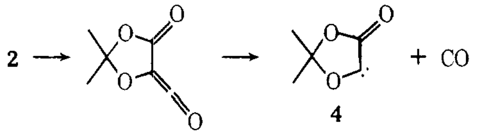
2 1

sealedPyrex bombs for 15 min. The products were separated and analyzed using standard vacuum line techniques and conventional spectroscopic characterization. All products were carefully compared with known materials. Pyrolysis of 0.29 mmol of 2 gave nitrogen (0.25 mmol), carbon monoxide (0.80 mmol), acetone (0.23 mmol), a small amount of carbon suboxide (0.003 mmol), and traces of propylene.



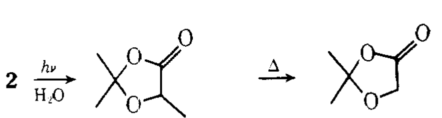
(1.0) (0.85) (2.7) (0.78) (0.01)

It is extraordinarily tempting to begin a mechanistic analysis of this reaction with the postulate that the first step in the decomposition of 2 is the Wolff rearrangement (in either the carbene 1 or 2 itself) to give ketene 3. Such a process is precedented in the gas-phase chemistry of carboalkoxycarbenes,[3] and ketene 3 is a likely source of carbon monoxide and the new carbene 4. This cleavage of a ketene to a carbene of type 4 is also known.[3]

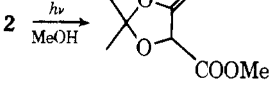


3 4

Ketene 3 can be trapped. Photolysis of 2 in benzene/water leads to the unstable β-keto acid 5 which, on heating or gas chromatography, decarboxylates to the known dioxolanone 6.[4] Although the decomposition of 5 could be followed by NMR spectroscopy, its instability prevented a quantitative analysis of its formation. However, irradiation of 2 in benzene/methanol resulted in the formation of the known[5] ester 7 in 69% yield.

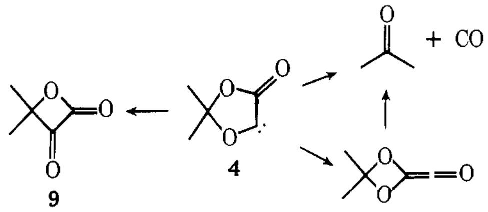


5 6



7

Thus the presence of ketene 3 is demonstrated, and its conversion to 4 seems very likely under the reaction conditions. Carbene 4 can either undergo direct cleavage to two more molecules of carbon monoxide and one of acetone, or undergo another Wolff rearrangement to 8, which could then yield carbon monoxide and acetone. Rearrangement to 9 seems less likely on the grounds that this path is not favored in the related decomposition of dicarbomethoxycarbene.[3]



9 4 8

The small amounts of propylene and carbon suboxide are more difficult to explain, although propylene could be formed by deoxygenation of acetone by any of the carbenes present in the reaction. Carbon suboxide is a possible product of direct fragmentation of 1, although this appears to be an unprecedented reaction.

Experimental Section

Synthesis of 2,2-Dimethyl-4,6-diketo-5-diazo-1,3-dioxane (Meldrum's Diazo). The procedure followed was similar to that reported by Eistert and Geiss.[6] Trimethylamine (8.4 g) was added dropwise to a solution of 11.6 g of Meldrum's acid[7] in 40 mL of ethanol. The solution was stirred in a dry ice/acetone bath until the temperature reached −15 °C. Tosyl azide (16 g) was slowly added, keeping the temperature below −10 °C. After 30 min of stirring, a yellow-orange solid precipitated. The solution was concentrated for 15 min on the rotary evaporator with no heat. It was cooled for 1 h in the dry ice/acetone bath at −20 °C and filtered. The yellow crystals were recrystallized twice from absolute alcohol at 0 °C to yield 7.4 g (50%), mp 93–95 °C.

Pyrolysis of Meldrum's Diazo. Meldrum's diazo (50 mg, 0.294 mmol) was pyrolyzed in a sealed Pyrex bomb (125 mL) at 320 °C in a molten salt ($NaNO_3/NaNO_2$) bath. The bombs were opened on a vacuum line and the products distilled into a trap at −196 °C. The products noncondensable at −196 °C (N_2 and CO) were injected into a 16-ft 13X molecular sieve column. Condensable products were distilled from a trap at −78 to −196 °C in order to separate the products further. Each of the fractions were analyzed by IR and gas chromatography on 6- and 20-ft dimethylsulfolane columns. All the products were identified by comparison of their physical characteristics (GC and IR) with those of authentic samples. The quantity of acetone was measured by calibration of the IR band at 1750 cm^{-1} and the carbon suboxide yields were measured following its IR band at 2260 cm^{-1}.

Photolysis of Meldrum's Diazo in Wet Benzene. Meldrum's diazo (170 mg, 0.001 mol) was dissolved in 12 mL of benzene and 0.1 mL of water. The emulsion was photolyzed for 18 h with a 450-W medium-pressure Hanovia mercury arc. The solution was filtered and the benzene evaporated to yield white crystals of β-keto acid 5.

Pyrolysis of 5. Pyrolysis in acetone-d_6 in a sealed Pyrex tube at 110 °C yields dioxolanone 6 quantitatively.

Photolysis of Meldrum's Diazo in Benzene and Methanol. Meldrum's diazo (170 mg) was dissolved in 12 mL of benzene and 0.1 mL of methanol. The solution was photolyzed as above for 18 h and the products were analyzed directly on a 10-ft, 10% Carbowax 20M column at 140 °C. The yield of ester 7 was estimated at 69% by use of dimethyl malonate as internal standard.

Registry No.—**2**, 7270-63-5; **5**, 62609-78-3; **6**, 4158-86-5; **7**, 62609-79-4; Meldrum's acid, 2033-24-1; tosyl azide, 938-10-3; nitrogen, 7727-37-9; carbon monoxide, 630-08-0; acetone, 67-64-1; carbon suboxide, 504-64-3.

References and Notes

(1) (a) Auburn University. (b) Princeton University. (c) We thank the Research Corporation[1a] and the National Science Foundation[1b] for support. One of us (S.L.K.) thanks Auburn University for support through an Auburn University Fellowship and Princeton University for support through the Office of the Dean of Student Affairs. Portions of this work are taken from the Ph.D. Thesis of S.L.K., Auburn University, 1974.

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