(3) was liberated immediately as a yellow oil, which was extracted with 40 ml of ligroin (bp 110–120 °C). To the boiling ligroin solution was added dropwise 1.61 g (13.5 mmol) of phenyl azide and the mixture was refluxed for 3 h. Fractional distillation of the reaction mixture gave 1.28 g (68%) of **4b:** bp 152–156 °C (0.03 mm); NMR ($CDCl_3$) δ 0.76 (d, 3, J = 7.5 Hz, C-3 CH_3), 1.78 (s, 3, C-4 CH_3), 3.49 (s, 3, NCH_3), 3.49 (q, 1, J = 7.5 Hz, C-3 H), 6.31 (s, 1, C-5 H), and 6.63–7.30 (m, 9, aromatic H).

Anal. Calcd for $C_{19}H_{20}N_2$: C, 82.57; H, 7.29; N, 10.14. Found: C, 82.38; H, 7.30; N, 10.31.

1,3,4-Trimethyl-2-benzoylimino-2,3-dihydro-1*H*-1-benzazepine (4c). In a similar manner as described above for **4b, 3** prepared from **2** (1.00 g, 4.5 mmol) was treated with benzoyl azide (1.29 g, 8.8 mmol) to give 1.10 g (80%) of **4c:** bp 158–162 °C (0.03 mm); NMR ($CDCl_3$) δ 0.81 (d, 3, J = 7.0 Hz, C-3 CH_3), 1.98 (s, 3, C-4 CH_3), 3.52 (s, 3, NCH_3), 3.82 (q, 1, J = 7.0 Hz, C-3 H), 6.38 (s, 1, C-5 H), and 6.80–8.20 (m, 9, aromatic H).

Anal. Calcd for $C_{20}H_{20}N_2O$: C, 78.92; H, 6.62; N, 9.20. Found: C, 78.63; H, 6.73; N, 9.25.

Hydrolysis of 4b or 4c. A solution of **4b** (550 mg, 2.0 mmol) in 5% potassium hydroxide in 50% ethanol (20 ml) was refluxed for 12 h. After removal of the ethanol, the aqueous solution was extracted with chloroform. The extract was washed with water, dried, and concentrated. Fractional distillation of the residue gave 65 mg (35%) of aniline and 362 mg (90%) of **5,** bp 105–109 °C (0.03 mm) [lit.[1] bp 103–105 °C (0.025 mm)].

In a similar manner, **4c** (257 mg, 0.84 mmol) gave 49 mg (48%) of benzamide and 158 mg (93%) of **5.**

1,3-Dimethyl-1,2-dihydroquinoline-2-spiro-2′-(1′-ethoxycarbonyl-3′-methyl)aziridine (8a). Ethyl azidoformate 0.96 g, 9.0 mmol) was added to a solution of **3** [prepared from 1.00 g (4.5 mmol) of **2**] in 40 ml of petroleum ether. The mixture was irradiated with a high-pressure mercury lamp (100 W) at 0–10 °C for 6 h. The solvent was removed under reduced pressure. Distillation of the residue gave 832 mg (74%) of **8a:** bp 118–125 °C (0.03 mm); ir (neat) 1708 cm^{-1}; NMR ($CDCl_3$) δ 0.86 (d, 3, J = 7.5 Hz, C-3′ CH_3), 1.37 (t, 3, J = 7.0 Hz, ethoxy CH_3), 2.16 (s, 3, C-3 CH_3), 3.14 (s, 3, NCH_3), 4.07 (q, 1, J = 7.5 Hz, C-3′ H), 4.32 (q, 2, J = 7.0 Hz, ethoxy CH_2), and 6.83–7.40 (m, 5, C-4 and aromatic H).

Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.32; H, 7.41; N, 10.34.

1,3-Dimethyl-1,2-dihydroquinoline-2-spiro-2′-(1′-phenyl-3′-methyl)aziridine (8b). In a similar manner as described for **8a,** a solution of **3** [prepared from 1.00 g (4.5 mmol) of **2**] and phenyl azide (1.08 g, 8.4 mmol) in petroleum ether was treated giving 772 mg (62%) of **8b:** bp 125–132 °C (0.03 mm); NMR ($CDCl_3$) δ 1.36 (d, 3, J = 7.5 Hz, C-3′ CH_3), 1.72 (s, 3, C-3 CH_3), 2.36 (s, 3, NCH_3), 4.28 (q, 1, J = 7. Hz, C-3′ H), and 6.40–7.48 (m, 10, C-4 and aromatic H).

Anal. Calcd for $C_{19}H_{20}N_2$: C, 82.57; H, 7.29; N, 10.14. Found: C, 82.43; H, 7.29; N, 10.28.

1,3-Dimethyl-1,2-dihydroquinoline-2-spiro-2′-(1′-benzoyl-3′-methyl)aziridine (8c). In a similar manner as described above for **8a,** treatment of **3** [prepared from 1.00 g (4.5 mmol) of **2**] with benzoyl azide (1.33 g, 8.4 mmol) gave 821 mg (60%) of **8c:** bp 143–149 °C (0.04 mm); ir (neat) 1660 cm^{-1}; NMR ($CDCl_3$) δ 0.82 (d, 3, J = 7.5 Hz, C-3′ CH_3), 2.23 (s, 3, C-3 CH_3), 2.98 (s, 3, NCH_3), 4.03 (q, 1, J = 7.5 Hz C-3′ H), and 6.73–8.05 (m, 10, C-4 and aromatic H).

Anal. Calcd for $C_{20}H_{20}N_2O$: C, 78.92; H, 6.62; N, 9.20. Found: C, 78.74; H, 6.64; N, 9.23.

Thermal Rearrangement of 8a, 8b, and 8c to 4a, 4b, and 4c. Five hundred milligrams of **8a, 8b,** or **8c** was sealed in a glass tube under reduced pressure and heated at 180 °C for 1 h. Distillation of the reactant gave 450 mg (90%) of **4a** [bp 138–142 °C (0.07 mm), lit.[1] bp 130–132 °C (0.03 mm)], 490 mg (98%) of **4b,** or 457 mg (91%) of **4c.** They were identified by spectroscopic comparisons with authentic samples obtained by the thermal reaction of **3** with ethyl azidoformate,[1] phenyl azide, or benzoyl azide, respectively.

Reaction of 1,3-Dimethyl-2-ethyl-1,2-dihydroquinoline[5] (1) with Phenyl Azide or Benzoyl Azide. Phenyl azide (4.76 g, 40 mmol) was added dropwise to a boiling solution of **1** (1.87 g, 10 mmol) in 20 ml of ligroin (bp 110–120 °C). The mixture was heated at reflux for 6 h. Fractional distillation of the reaction mixture was repeated to give 1.11 g (40%) of **4b,** which was identified with an authentic sample prepared by the thermal reaction of **3** with phenyl azide.

A similar treatment of **1** (1.87 g, 10 mmol) with benzoyl azide (5.88 g, 40 mmol) gave 3.82 g (80%) of phenyl isocyanate and 1.83 g (98%) of **1.**

Registry No.—**1,** 51904-95-1; **2,** 55539-76-9; **3,** 57091-72-2; **4b,** 59181-48-5; **4c,** 59183-03-5; **5,** 57091-65-3; **8a,** 59181-49-6; **8b,** 59813-04-6; **8c,** 59181-51-0; phenyl azide, 622-37-7; benzoyl azide, 582-61-6; ethyl azidoformate, 817-87-8.

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A General Method for the Synthesis of Reactive α,β-Unsaturated Diazomethyl Ketones: Allenyl Diazomethyl Ketone and Vinyl Diazomethyl Ketone[1]

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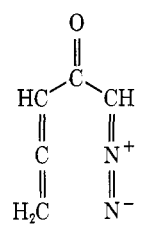
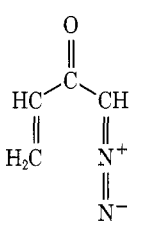
In the course of our photochemical studies, we required two unknown α,β-unsaturated diazomethyl ketones, allenyl diazomethyl ketone (**1**) and vinyl diazomethyl ketone (**2**).



1

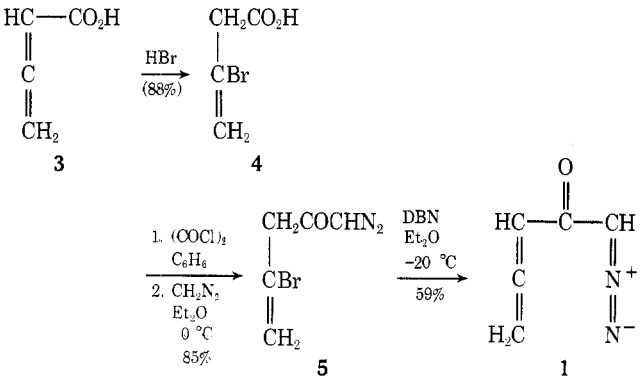


2

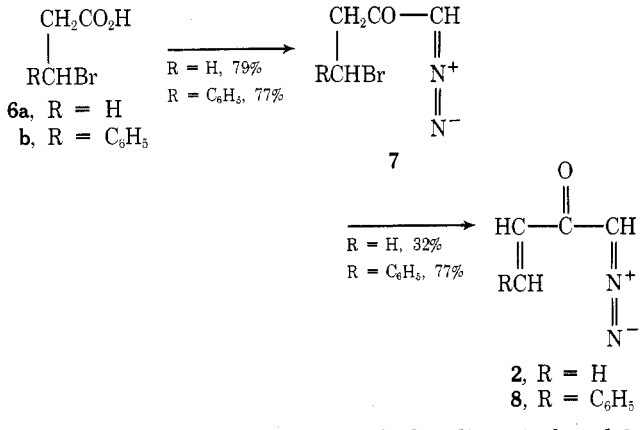
Synthesis of α,β-unsaturated diazomethyl ketones poses special problems. The Arndt–Eistert reaction of diazomethane with α,β-unsaturated acid chlorides does not compete effectively with the cycloaddition of diazomethane to the conjugated double bond.[2,3] The normal Arndt–Eistert reaction prevails only in a few highly substituted α,β-unsaturated acid chlorides.[3–6] Alternative procedures based on diazo transfer,[2,7] tosylhydrazone anion decomposition,[8] and the modified Forster[9] reaction have been developed for certain α,β-unsaturated diazo ketones. We wish to describe a facile method for the conversion of α,β-unsaturated carboxylic acids to the corresponding α,β-unsaturated diazomethyl ketones which is applicable to the synthesis of even the most reactive α,β-unsaturated diazomethyl ketones. The method uses a protected double bond in the Arndt–Eistert reaction and takes advantage of the stability of diazomethyl ketones in base in the regeneration of the double bond.

Addition of hydrogen bromide to 2,3-butadienoic acid (**3**)[10] gives 3-bromo-3-butenoic acid (**4**). Successive treatment of **4** with oxalyl chloride and diazomethane gives **5** which on treatment with DBN (1,5-diazabicyclo[4.3.0]non-5-ene)[11] in ether at −20 °C gives allenyl diazomethyl ketone (**1**). The maximum yield of allenyl diazomethyl ketone (**1**) was obtained when **5** was treated with 1 equiv of DBN in ether at −20 °C followed by warming to room temperature over 20 min. Use of potassium *tert*-butoxide in ether gave a lower yield of **1.**

A similar sequence starting from 3-bromopropionic acid (**6a**) gives vinyl diazomethyl ketone (**2**) via **7a.** Vinyl diazomethyl ketone proved to be very reactive at room temperature. It forms a glassy solid in 30 min at room temperature even in



the absence of light and oxygen. The utility of our method for substituted vinyl diazomethyl ketones is illustrated by the



synthesis of the previously described 1-diazo-4-phenyl-3-buten-2-one (8)[7,9] from commercially available 3-bromo-3-phenylpropionic acid.

Experimental Section

3-Bromo-3-butenoic Acid (4). Anhydrous hydrogen bromide was passed for 3 min into a stirred solution of **3**[10] (3.75 g, 0.0447 mol) in 150 ml of anhydrous ether at 0 °C. Removal of the solvent and excess acid under reduced pressure gave a solid residue, which when recrystallized from hexane gave **4** (6.5 g, 88%) as white platelets: mp 45.5–47 °C (lit.[12] mp 46–47 °C); ir ($CHCl_3$) 1720 (s, C=O), 1634 cm^{-1} (m, C=C); ^1H NMR ($CDCl_3$) δ 3.54 (d, 2 H, J = 1 Hz, CH_2), 5.64 (d, 1 H, J = 2 Hz, vinyl H), 5.78 (m, 1 H, vinyl H); molecular ion m/e 164 and 166.

Anal. Calcd for $C_4H_5BrO_2$: C, 29.12; H, 3.05; Br, 48.43. Found: C, 29.33; H, 3.10; Br, 48.22.

4-Bromo-1-diazo-4-penten-2-one (5). A solution of **4** (3.30 g, 0.02 mol) and oxalyl chloride (2.8 g, 0.022 mol) in benzene (12 ml) was stirred at 38 °C until the ir spectrum of the solution showed no acid carbonyl bond (12–14 h). About 20% of the solvent was removed under vacuum, and the solution was added rapidly to a vigorously stirred solution of diazomethane (2.0 g, 0.048 mol) in 170 ml of ether at 0 °C. After 10 min of stirring, removal of the ether under reduced pressure at 0 °C gave an orange liquid. Distillation in a cold finger still at 0.1 mm with pot temperature 50–75 °C gave **5** (3.21 g, 85%) as a yellow liquid: ir ($CHCl_3$) 2110 (s, C=N_2), 1642 (s, C=O), 1360 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 3.48 (d, 1 H, J < 1 Hz, CH_2), 5.48 (s, 1 H, CHN_2), 5.66 (d, 1 H, J = 2 Hz, vinyl H), 5.80 (m, 1 H, vinyl H); no molecular ion observable, fragment ion m/e 147 and 149 (loss of CHN_2).[13]

4-Bromo-1-diazo-2-butanone (7a). 3-Bromopropanoic acid (4.59 g, 0.03 mol) was reacted by the procedure described for the preparation of **5**. The product was distilled in a short-path still to give **7a** (4.2 g, 79%) as a yellow liquid: bp 43 °C (0.03 mm); ir ($CHCl_3$) 2112 (s, C=N_2), 1640 (s, C=O), 1375 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 2.88 (t, 2 H, J = 6 Hz, CH_2), 3.58 (t, 2 H, J = 6 Hz, CH_2), 5.36 (s, 1 H, CHN_2), splitting is observable in each peak of the triplets; molecular ion m/e 175.9591 (calcd for $C_4H_5BrN_2O$, 175.9586).[13]

4-Bromo-1-diazo-4-phenyl-2-butanone (7b). 3-Bromo-3-phenylpropanoic acid (5.73 g, 0.025 mol) was reacted by the procedure described for the preparation of **5**, except that the acid chloride was formed at 50 °C. The product, a yellow solid, when recrystallized from ⅙ benzene/hexane gave **7b** (4.87 g, 77%) as light yellow needles: mp 68.5–70 °C; ir ($CHCl_3$) 2110 (s, C=N_2), 1642 (s, C=O), 1378 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 3.14 (d, 1 H, J = 6 Hz, CH_2), 3.22 (d, 1 H, J = 8 Hz, CH_2), 5.21 (s, 1 H, CHN_2), 5.41 (d of d, 1 H, J = 8 and 6 Hz, CH), 7.32 (broad s, 5 H, phenyl); molecular ion m/e 252 and 254.

Anal. Calcd for $C_{10}H_9BrN_2O$: C, 47.45; H, 3.58; Br, 31.57; N, 11.09. Found: C, 47.76, H, 3.57; Br, 31.72; N, 11.04.

1-Dizao-3,4-pentadien-2-one (1). A solution of **5** (0.672 g, 0.0035 mol) and hydroquinone (0.02 g) in 40 ml of anhydrous ether was cooled to −20 °C under N_2. With vigorous stirring, freshly distilled DBN (0.435 g, 0.0035 mol) was added dropwise over 1 min. A precipitate formed immediately. The solution was warmed to room temperature over 20 min and filtered, and the solvent was removed under vacuum at 0 °C giving a yellow liquid. The flask containing the liquid was immediately connected to a U-tube leading to a vacuum pump. With the tube at 15 °C the system was evaporated to 0.1 mm, and the flask was warmed over 15 min to 70 °C. The product (**1**, 0.224 g, 59%) was collected as a yellow liquid: ir ($CHCl_3$) 2112 (s, C=N_2), 1968 and 1935 (m, C=C=C), 1620 (s, C=O), 1368 cm^{-1} (s); ^1H NMR δ 5.20 (broad d, 2 H, J = 7 Hz, allenyl CH_2), 5.52 (s, 1 H, CHN_2), 5.71 (d of d, 1 H, J = 7 and 8 Hz, allenyl CH) (the allenyl ^1H NMR pattern is similar to that of **3**); molecular ion (**1**) m/e 108.0331 (calcd for $C_5H_4N_2O$, 108.0324).[13] The product (**1**) could be kept for a few days at −30 °C. Allenyl diazomethyl ketone (**1**, 0.025 g) could be chromatographed on activity III alumina (2.0 g) with rapid elution by 20% benzene in pentane (75% recovery). Alumina of greater activity entirely decomposed **1**.

1-Diazo-3-buten-2-one (2). Reaction of **7a** (1.33 g, 0.0075 mol) and DBN (0.930 g, 0.0075 mol) by the method used to prepare **1** gave, upon removal of solvent, a yellow liquid. This liquid was immediately transferred to a 5-ml pear-shaped flask fitted with a N_2 capillary ebullator and connected through a cold trap to a vacuum pump. The system was protected from light. The trap was cooled to −7 °C, the system evacuated to 0.1 mm, and the flask warmed over 10 min to 35 °C. The product (**2**, 0.23 g, 32%) was collected as a yellow liquid: ir ($CHCl_3$) 2100 (s, C=N_2), 1645 (s, C=C), 1610 (s, C=O), 1348 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 5.34 (s, 1, CHN_2), 5.56 (d of d, 1 H, J = 5 and 7 Hz, vinyl CH), 6.22, 6.19, and 6.11 (m, 2 H, vinyl CH_2) (the vinyl CH_2 pattern is interpretable as two doublets, with their upfield peaks superimposed; the olefin ^1H NMR pattern is similar to that of 3-buten-2-one); molecular ion (**2**) m/e 96.0326 (calcd for $C_4H_4N_2O$, 96.0324).[13] The product (**2**) decomposed significantly in 2 days when stored at −30 ° C.

1-Diazo-4-phenyl-3-butene-2-one (8). Reaction of **7b** (1.52 g, 0.006, mol) and DBN (0.758 g, 0.0061 mol) using the procedure for the preparation of **2** gave, on removal of solvent, a yellow solid, which when recrystallized from hexane gave **8** (0.79 g, 77%) as yellow needles: mp 66.5–68.5 °C (lit.[9] mp 68–69 °C); ir ($CHCl_3$) 2102 (C=N_2), 1642 (C=C), 1592 cm^{-1} (C=O).

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Registry No.—**1**, 59813-08-0; **2**, 59813-09-1; **3**, 5732-10-5; **4**, 21031-45-8; **5**, 59813-10-4; **6a**, 590-92-1; **6b**, 15463-91-9; **7a**, 59813-11-5; **7b**, 59813-12-6; **8**, 24265-71-2; oxalyl chloride, 79-37-8; diazomethane, 334-88-3; DBN, 3001-72-7.

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