($CDCl_3$) δ 2.66–2.86 (unresolved m, 4 H, allylic protons), 3.47 (s, 6 H, methoxy protons), 4.58 (br t, 2 H, vinylic protons, $J \approx 3$ Hz).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.74; H, 8.80.

The following procedures, describing the preparation of compounds **5** (R = $CH_2CH_2CH{=}CH_2$) and **2** (R = $CH_2CH_2CH{=}CH_2$), are typical.

3-(Δ^3-Butenyl)-2,4-dimethoxy-1,4-cyclohexadiene (5, R = $CH_2CH_2CH{=}CH_2$). To a solution of *t*-BuLi[10] (1.11 equiv) in cold (−78 °C) THF (80 mL) was added 1.98 g of 1,5-dimethoxy-1,4-cyclohexadiene (**3**) and the resultant solution was stirred at −78 °C for 1 h. HMPA (1.17 equiv, freshly distilled from $LiAlH_4$) was added and stirring was continued for an additional 10 min. Addition of 4-bromo-1-butene (1.31 equiv, freshly filtered through a short column of neutral alumina) resulted in an immediate change in the color of the reaction mixture (maroon to light brown). The reaction mixture was allowed to warm to room temperature, diluted with 50 mL of brine, and then trice extracted with 50-mL portions of pentane. The combined pentane extracts were washed twice with brine and dried over anhydrous $MgSO_4$. Removal of the solvent, followed by distillation (air-bath temperature 55–60 °C, 0.1 Torr) of the resultant light brown oil, afforded 1.71 g (99%) of 3-(Δ^3-butenyl)-2,4-dimethoxy-1,4-cyclohexadiene: IR (film) ν_{max} 3090, 3020, 2950, 2925, 2850, 1690, 1660, 1640, 1610, 1450, 1390, 1320, 1300, 1140, 1020, 985, 955, 900, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70–2.02 (unresolved m, 4 H, $-CH_2CH_2CH{=}CH_2$), 2.66–3.04 (unresolved m, 3 H, C-3 and C-6 protons), 3.50 (s, 6 H, methoxy protons), 4.68 (t, 2 H, C-1 and C-5 protons, J = 4 Hz), 4.76–5.06 (unresolved m, 2 H, $-CH{=}CH_2$), 5.56–6.02 (unresolved m, 1 H, $-CH{=}CH_2$).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.00; H, 9.38.

2-(Δ^3-Butenyl)-1,3-cyclohexanedione (2, R = $CH_2CH_2CH{=}CH_2$). To a solution of compound **5** (R = $CH_2CH_2CH{=}CH_2$) (0.52 g) in acetone (12 mL, spectrograde, previously purged with a stream of N_2 for 15 min) was added, with vigorous stirring, 1 N hydrochloric acid (4 mL, previously purged with a stream of N_2 for 15 min). The resultant solution was stirred for 1 h. The acetone was removed under reduced pressure, the residue was diluted with 10 mL of brine, and the mixture was then extracted four times with 10-mL portions of CH_2Cl_2. The combined extracts were dried over anhydrous magnesium sulfate. Removal of the solvent afforded 0.42 g (95%) of 2-(Δ^3-butenyl)-1,3-cyclohexanedione as a white crystalline solid. This material was shown by GLC analysis to be >98% pure,and exhibited IR and ^1H NMR spectra which were essentially identical with those of an analytical sample obtained by recrystallization from benzene–heptane: mp 95–96 °C (lit. mp 95–97.5 °C[4], 92.5–93.5 °C[6]); UV (C_2H_5OH) λ_{max} 262 mm (ϵ 1.56 × 10^4); IR ($CHCl_3$) ν_{max} 3570, 3500–2600 (broad), 1715, 1695, 1615, 1370, 1170, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.74–2.28 (m, 4 H), 2.28–2.76 (m, 6 H), 3.45 (t, 1/6 H, C-2 proton of diketo tautomer, J = 5 Hz), 4.84–5.16 (unresolved m, 2 H, $-CH{=}CH_2$), 5.62–6.12 (unresolved m, 1 H, $-CH{=}CH_2$).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.27; H, 8.45.

Acknowledgments. Financial support from the National Research Council of Canada is gratefully acknowledged.

Registry No.—**3**, 37567-78-5; *m*-dimethoxybenzene, 151-10-0.

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Aliphatic Diazo Ketones. A Modified Synthesis Requiring Minimal Diazomethane

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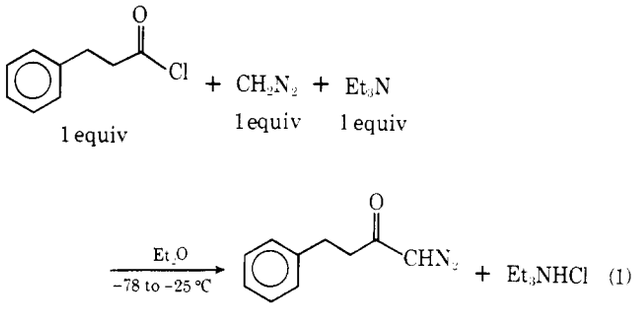
The common practice of employing excess diazomethane to scavenge HCl during the preparation of α-diazo ketones from acid chlorides and diazomethane[1] works extremely well in most instances but does not lend itself to the efficient use of isotopically labeled diazomethane or of other diazoalkanes. To circumvent this problem, Newman[2] and Berenbom[3] independently developed an alternative procedure for preparing α-diazo ketones from aromatic acid chlorides using 1 molar equiv of diazomethane in the presence of triethylamine at 0 °C. Under the same conditions, however, aliphatic acid chlorides bearing α-hydrogen atoms give only low yields of impure products,[2] presumably as a consequence of competing ketene formation and subsequent side reactions.[4]

In connection with a ^{13}C-labeling study, we had need to prepare the diazo ketone derived from 3-phenylpropanoyl chloride using minimal diazomethane and found that this can be accomplished simply by carrying out the reaction with triethylamine present at lower temperatures than usual (eq 1). A stoichiometric ratio of reagents gives optimal yields of



the diazo ketone based on diazomethane (see Table I). By comparison, the conventional procedure,[1] using 2 equiv of diazomethane, gives a much lower yield of product based on diazomethane (49.6%), albeit in a somewhat higher state of purity (95.2% by N_2 evolution, 90.1% by NMR). Chromatography on silica gel provides a means of separating and identifying the minor by-products formed during the reaction in eq 1 (see Experimental Section); however, the crude product proved satisfactory for subsequent copper-catalyzed cyclization.[5]

Table I lists several other aliphatic diazo ketones prepared by this method. Ketene formation competes successfully only in those cases with especially acidic α-hydrogens; phenylacetyl chloride, for example, gives an 85% yield of 2- and 3- phenylcyclobutanone under these reaction conditions,[6] presumably via phenyl ketene and phenylcyclopropanone.[7]

Experimental Section

1-Diazo-4-phenyl-2-butanone. Dry triethylamine[8] (11.1 mL, 0.08 mol) was added to 350 mL of an anhydrous ethereal solution of diazomethane[9] (0.08 mol) under nitrogen in a baked-out 1-L Morton flask fitted with a mechanical stirrer, a dropping funnel, and a low-temperature thermometer. The solution was cooled to − 78 °C (dry ice/acetone), and 11.8 mL of 3-phenylpropanoyl chloride[10] (0.08 mol) in 40 mL of anhydrous ether[8] was added dropwise with vigorous stirring over 25 min. A thick slurry formed during the addition.[11] The reaction mixture was stirred an additional 15 min at −78 °C and then for 1 h at −25 to −20 °C (dry ice/H_2O/$CaCl_2$).[12] During the course of the

Table I. Aliphatic Diazo Ketones Prepared by the Method [a] of eq 1

Registry no.	Diazo ketone	Yield, %	Purity, % N_2 evol (NMR)
10290-42-3	$C_6H_5CH_2CH_2C(=O)CHN_2$	96	82 (83)
31151-40-3	c-$C_6H_{11}C(=O)CHN_2$	96	85 (77)
58697-26-0	$CH_3(CH_2)_7C(=O)CHN_2$	96	87 (85)
14088-55-2	$(CH_3)_2CHC(=O)CHN_2$	86[b]	85 (76)
	$C_6H_5CH_2C(=O)CHN_2$		(<10%)

[a] Optimized only for the first entry. [b] Lower yield due to partial solubility of the product in water.

reaction, the mixture grew more viscous and then thinned out again. After warming to room temperature, the reaction mixture was diluted with water. The organic layer was separated and washed successively with 10% aqueous acetic acid, water, saturated sodium bicarbonate solution, water, and saturated sodium chloride solution. The resulting solution was dried over calcium sulfate[13] and concentrated under vacuum to a deep yellow oil: 12.8–13.9 g, 92–100% yield.

A weighed aliquot of the crude product was dissolved in ethanol and treated with concentrated hydrochloric acid;[2,3] the nitrogen evolved corresponded to 76–87% of that expected for pure diazo ketone. NMR analysis of the crude product revealed 1-diazo-4-phenyl-2-butanone (76–90%), 1-chloro-4-phenyl-2-butanone (4–5%), methyl 3-phenylpropanoate (2–3%), 3-phenylpropanoic anhydride, and benzylcyclobutanone (both isomers), all of which were isolated by chromatography on silica gel (15% ethyl acetate/petroleum ether) for identification purposes.

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Registry No.—Diazomethane, 334-88-3; 3-phenylpropanoyl chloride, 645-45-4; 1-chloro-4-phenyl-2-butanone, 20845-80-1; methyl 3-phenylpropanoate, 103-25-3; cyclohexylcarbonyl chloride, 2719-27-9; nonanoyl chloride, 764-85-2; 2-methylpropanoyl chloride, 79-30-1.

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(8) Distilled under nitrogen from sodium/benzophenone.
(9) Caution Explosive. Diazomethane was prepared according to the procedure of J. A. Moore and D. E. Reed, "Organic Syntheses", Collect. Vol. V, 1973, 351, and standardized by duplicate titrations according to the procedure of F. Arndt, "Organic Syntheses," Collect. Vol. II, 1943, p 165. Reagent grade ether (ethanol free) must be used to avoid contamination of the final product by ethyl ester. After distillation, the diazomethane solution still contains at least 1% water which can be removed by drying over potassium hydroxide pellets for 30 min at 0 °C. Omission of this drying step leads to a considerable amount of methyl ester in the final product. When properly dried, no cloudiness (ice crystals) developes in the ethereal diazomethane on cooling to −78 °C; further drying over sodium wire proved unnecessary.
(10) Prepared from hydrocinnamic acid and thionyl chloride in 95% yield after distillation.
(11) Even in the absence of diazomethane, a thick white precipitate forms instantly. Hydrolysis of the resulting mixture gives hydrocinnamic anhydride, the expected product from an acylammonium salt. [See J. V. Paukstelis and M.-g. Kim, *J. Org. Chem.*, **39**, 1503 (1974)]. The reactive species may actually be this acylammonium salt, although formation of the diazo ketone does not occur at −78 °C.
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A Convenient Large-Scale Preparation of Benzobarrelene

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Benzobarrelene (**1**) is a molecule of considerable potential mechanistic interest, but studies of its chemistry have been few on account of its relative unavailability. Neither of the existing synthetic routes, the addition of benzyne to benzene,[1] nor the cycloaddition of maleic anhydride to β-naphthol,[2] is suitable for large-scale preparation. However, Heaney and co-workers have recently reported[3] a high-yield preparation which consists of the reductive dechlorination of tetrachlorobenzobarrelene, obtained from the cycloaddition of tetrachlorobenzyne to benzene. We now present here an alternative large-scale preparation of benzobarrelene which has considerable flexibility and should allow efficient isotopic labeling of the bicyclic skeleton, as well as preparation of aromatic substituted derivatives.

The addition of dichlorocarbene to the readily available benzonorbornadiene (**2**)[4] gives a rearranged adduct which on reductive dechlorination affords benzo[6,7]bicyclo[3.2.1]-octa-2,6-diene (**4**).[5] In the present work, the method of Parham and Schweizer[6] was used for generating dichlorocarbene. Dechlorination of the adduct was effected with sodium and *tert*-butyl alcohol (Scheme I) and **4** was obtained in an overall yield of 80% for the two steps.

Bromination of hydrocarbon **4** in dichloromethane at −20 °C proceeded with rearrangement to give di-*anti*-bromo adduct **5** in essentially quantitative yield. This key step serves both to bring about the requisite skeletal rearrangement and to provide the functionality which permits the easy introduction of two double bonds. The structure of adduct **5** was securely assigned from its ^1H and ^{13}C NMR spectra (see Experimental Section) which unambiguously provide evidence for the symmetry of the molecule. Analogous stereospecific bromination rearrangements have been observed for the homologues, benzonorbornadiene (**2**)[7] and benzo[7,8]bicyclo[4.2.1]nona-2,7-diene,[8] and present no particular mechanistic problems.

In the final step, the double dehydrobromination of **5** was achieved with surprising efficiency using the classical method of potassium *tert*-butoxide in tetrahydrofuran. Essentially pure benzobarrelene was isolated in yields greater than 90%, after sublimation. Benzobarrelene (**1**) may thus be prepared

Scheme I