and 25 mL of a 1 M solution B_2H_6 in THF was added dropwise. After warming to room temperature, the excess hydride was decomposed by dropwise addition of water. The organoborane was oxidized at 30–50 °C (water bath) by the addition of 12 mL of 3 N NaOH, followed by dropwise addition of 12 mL of 30% H_2O_2. After 1 h 30 g of potassium carbonate was added. The THF layer was separated, and the aqueous phase was extracted with THF. The THF extracts were combined and dried. Following the removal of the solvent by rotary evaporation, the product was purified by vacuum distillation (bp 105–106 °C/2 mm) in a 60% yield.

2,3-Dinonadecyl-1,4-butanediol (5b) was prepared in the same manner as **5a** by using 0.85 mmol of **3e** in 75% yield after recrystallization from ether (mp 60–61 °C. Anal. Calcd $C_{42}H_{86}O_2$: C, 80.95; H, 13.91; O, 5.13. Found: C, 80.75; H, 13.71; O, 5.34.

Acknowledgment. We acknowledge financial support from the National Science Foundation, Polymers Program (Grant No. DMR 8214211).

Registry No. **1**, 513-81-5; **2**, 69780-62-7; **3c**, 84652-75-5; **3d**, 92882-24-1; **3e**, 92882-25-2; **4**, 92739-56-5; **5a**, 57716-80-0; **5b**, 92882-26-3; *n*-butylbromide, 109-65-9; 1-bromododecane, 143-15-7; 1-bromooctadecane, 112-89-0; ethylene oxide, 75-21-8; 2,3-dimethyl-1,3-butadiene, 513-81-5.

Michael Addition to 1,3-Bis(alkoxycarbonyl)allenes: Synthesis of Heterocyclic Compounds Having Glutaconate Structure in the Molecules

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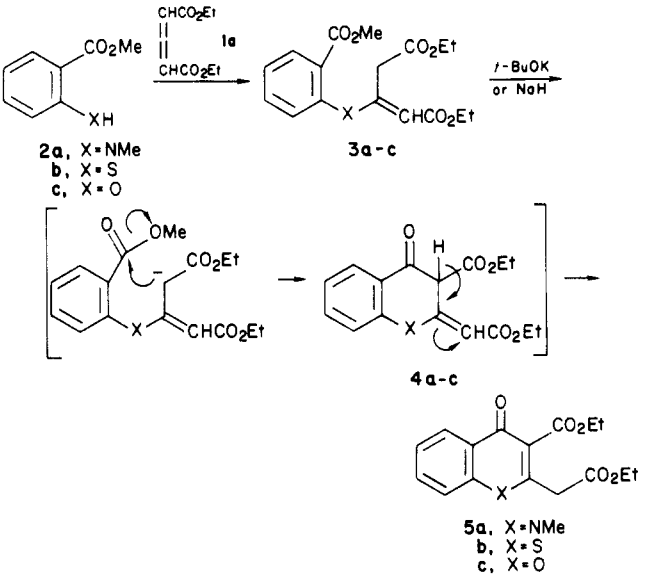
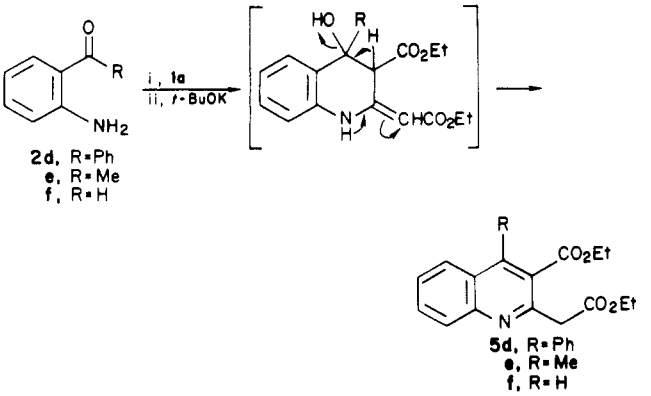
The use of 1,3-dicarbalkoxyallene **1** in the Diels–Alder reaction has been proven to be valuable for the construction of cyclic compounds containing a glutaconate system.[1] Although **1** is also expected to be a useful receptor toward Michael addition, the synthetic applications of such allenes have been limited to a few examples.[2,3] A recent paper[3] on the synthetic utility of **1** by Michael reaction with salicylaldehyde, *o*-hydroxyacetophenone, and methyl salicylate prompted us to publish our own results on the Michael reaction of **1** with a variety of compounds having both nucleo- and electrophilic functional groups. This method provides a versatile route to heterocycles containing the glutaconate system.[4] This approach for the synthesis of these heterocycles is based on the presumption that compounds **2** having both nucleo- and electrophilic substituents at appropriate positions would first nucleophilically add to the allenic bond of 1,3-dicarbalkoxyallene **1** to form Michael-type adducts **3**. Subsequent base-catalyzed intramolecular cyclization to the electrophilic group of **3**, followed by isomerization under the conditions used, then would give the desired heterocycles **5** (Scheme I).

Reaction of equimolar amounts of methyl *N*-methylanthranilate (**2a**, X = NMe) with 1,3-dicarbethoxyallene (**1a**) in chlorobenzene at 100 °C for 30 min gave an adduct (**3a**) which, when treated with 1 equiv of potassium *tert*-butoxide at 0 °C for 5 min, resulted in the loss of the methoxy group to provide ethyl 3-carbethoxy-1-methyl-4(1*H*)-quinolinone-2-acetate (**5a**) in 65% overall yield. The double bond of the product appears to be in the endocyclic form (**5a**) rather than the tautomeric exocyclic form (**4a**) since the NMR spectrum exhibited two equivalent protons attributable to a CH_2CO_2Et group at 3.95 ppm. In the case of methyl thiosalicylate (**2b**, X = S) and methyl salicylate (**2c**, X = O), the reactions were accomplished at 0 °C by treatment with equimolar amounts of **1a** in tetrahydrofuran (THF) in the presence of 1 equiv of NaH to give the corresponding chromone-2-acetates (**5b** and **5c**). The use of *tert*-butoxide instead of NaH in the reaction of **2b**,**c** with **1a** gave lower yields.



o-Aminobenzophenone (**2d**), *o*-aminoacetophenone (**2e**), and *o*-aminobenzaldehyde (**2f**) reacted with **1a** in a similar



fashion as described for the reaction of **2a** with **1a** except that the cyclization was followed by dehydration. Thus, condensation of **2d–f** with **1a** in chlorobenzene at 80 °C for 30 min gave the adducts, which were treated with 1

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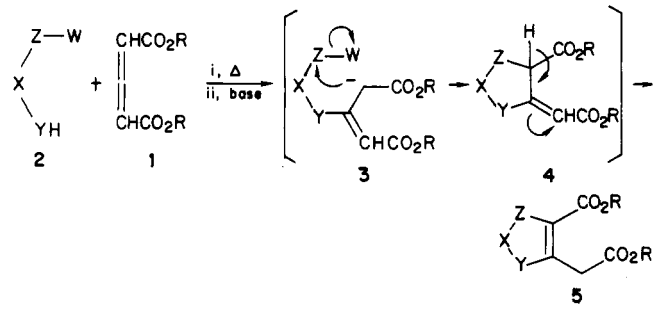
0022-3263/85/1950-1542$01.50/0

Table I. Michael Reaction of 1,3-Dicarbethoxyallene (1a)

product	reaction conditions[a]	yield, %	mp,[b] °C (recryst solvent) [bp,[b] °C (torr)]
5a	method A; 100 °C, 30 min; 0 °C, 5 min	65	107–108 (ethyl acetate–*n*-hexane)
5b	method C; 0 °C, 30 min	66	106–107 (ethyl acetate–*n*-hexane)
5c	method C; 0 °C, 2 h	29	[150 (0.07)[c]]
5d	method A; 80 °C, 30 min; 0 °C, 10 min	84	123–125[d] (ethanol); lit.[5] 121–122
5e	method A; 80 °C, 30 min; 0 °C, 10 min	63	140–143[d] (ethanol)
5f	method A; 80 °C, 30 min; 0 °C, 10 min	52	64.5–66.5 (*n*-hexane); lit.[6] 62
5g	method B; 0 °C, 10 min	51	83–86 (*n*-hexane)
5h	method B; rt, 1.5 h[e]	56	55 (*n*-hexane)
5i	method A; 80 °C, 1 h; 0 °C, 10 min	93	63–66 (ether–*n*-hexane); lit.[7] 67.5–68
5j	method A; 80 °C, 1 h; 0 °C, 10 min	20	[185 (0.05)[c]]

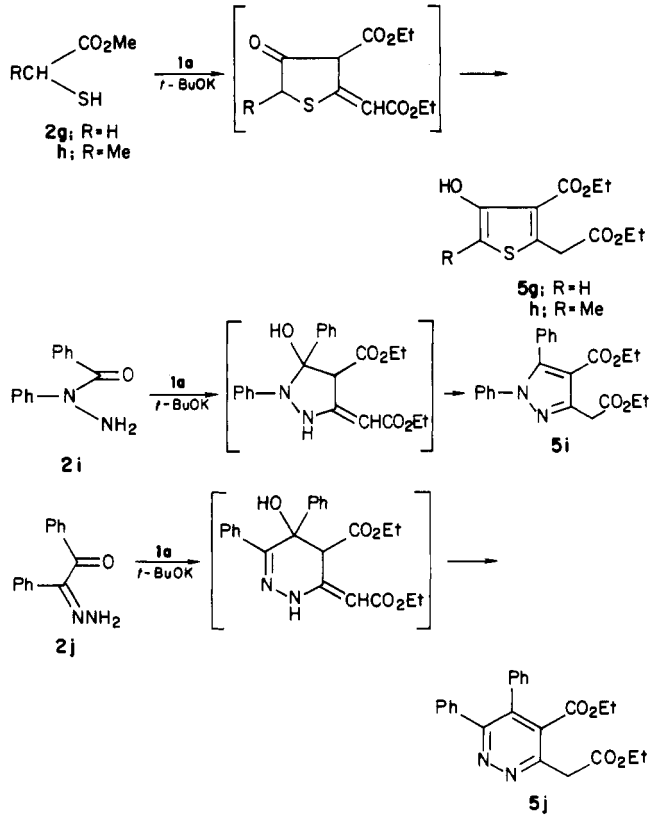
[a] See Experimental Section. [b] Uncorrected melting and boiling points are given. [c] Bath temperature. [d] Melting point of the picrate is given. [e] rt = room temperature.

Scheme I



equiv of potassium *tert*-butoxide at 0 °C for 10 min to give the corresponding dehydrated, cyclized products **5d–f** in good yields.

Allene (**1a**) is also attacked by aliphatic compounds having both nucleo- and electrophilic groups in the molecules. This provides a variety of monocyclic heterocycles containing the glutaconate system. Methyl thioglycolate (**2g**), methyl α-mercaptopropionate (**2h**), phenyl benzoylhydrazine (**2i**), and benzoin monohydrazone (**2j**) reacted with **1a** in the presence of potassium *tert*-butoxide



to give the corresponding cyclized products **5g–j**. Stable heterocycles having aromatized thiophene, pyrazole, and pyridazine rings were obtained as the final products in these reactions.

The structures of unknown compounds (**5a–c**, **5e**, **5g**, **5h**, and **5j**) were proven by microanalyses and IR, NMR, and mass spectral data. All known products (**5d**, **5f**, and **5i**) were identified by comparison with reported physical and spectral data. The reaction conditions, yields, and physical data of the products **5a–5j** are summarized in Table I. The present method of annulation using **1** provides a variety of heterocycles having the glutaconate system, which are otherwise difficultly obtainable. Moreover, the three individual reaction steps (Michael addition, ring closure, and isomerization or elimination) can be performed in a one-pot operation.

Experimental Section[8]

General Procedure for Michael Reaction of 1,3-Dicarbethoxyallene (1a). Method A. Typically, a solution of **1a** (184 mg, 1 mmol) and **2** (1 mmol) in chlorobenzene (2 mL) was heated for the period of time and at the temperature indicated in Table I. The solution was then cooled to 0 °C, and potassium *tert*-butoxide (112 mg, 1 mmol) was added. The mixture was stirred at 0 °C for several minutes and then partitioned between ethyl acetate and brine. The organic phase was dried over magnesium sulfate and evaporated in vacuo to give **5**. In many cases, the crude products required purification by column chromatography on silica gel using ethyl acetate–*n*-hexane (1:1.5–8) as eluting solvent or by recrystallization using the solvent indicated in Table I.

Method B. A suspension of **2** (1 mmol) and potassium *tert*-butoxide (1 mmol) in chlorobenzene (3.5 mL) was stirred at room temperature for 10 min and then cooled to 0 °C. A solution of **1a** (1 mmol) in chlorobenzene (1.5 mL) was added to the suspension, and the mixture was stirred by using the conditions indicated in Table I. Workup as described for method A gave **5**.

Method C. A suspension of **2** (1 mmol) and NaH (60% in mineral oil, 40 mg, 1 mmol) in THF (20 mL) was stirred at 0 °C for 5 min. A solution of **1a** (1 mmol) in THF (3 mL) was added dropwise to the suspension, and the mixture was stirred by using the conditions indicated in Table I. Workup as described for method A gave **5**.

Ethyl 3-carbethoxy-1-methyl-4(1*H*)-quinolone-2-acetate (5a) was prepared from **1a** (1 mmol) and **2a** (165 mg, 1 mmol) by method A and was purified by recrystallization.

Anal. Calcd for $C_{16}H_{19}NO_5$: C, 64.34; H, 6.04; N, 4.41. Found: C, 64.31; H, 6.01; N, 4.23.

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(8) IR absorption spectra were recorded on a JASCO IRA-1 spectrometer; and ^1H NMR spectra on one of the following spectrometers: Hitachi R-20A (60 MHz), Hitachi R-22 (90 MHz) with tetramethylsilane as an internal standard; and low- and high-resolution mass spectra on a JEOL JMS D-300 instrument with a direct-inlet system. Molecular ion peaks were observed for all products.

Ethyl 3-carbethoxythiochromone-2-acetate (5b) was prepared from **1a** (1 mmol) and **2b** (168 mg, 1 mmol) by method C and was purified by recrystallization.

Anal. Calcd for $C_{16}H_{16}O_5S$: C, 59.98; H, 5.03. Found: C, 59.79; H, 4.94.

Ethyl 3-carbethoxychromone-2-acetate (5c) was prepared from **1a** (1 mmol) and **2c** (152 mg, 1 mmol) by method C. Column chromatography gave pure **5c**; exact mass calcd for $C_{16}H_{16}O_6$ 304.0945, found 304.0939.

Ethyl 3-carbethoxy-4-phenylquinoline-2-acetate (5d) was prepared from **1a** (3 mmol) and **2d** (591 mg, 3 mmol) by method A. Column chromatography gave pure **5d**, identical in all respects with an authentic sample.

Ethyl 3-carbethoxy-4-methylquinoline-2-acetate (5e) was prepared from **1a** (3 mmol) and **2e** (405 mg, 3 mmol) by method A. Column chromatography gave pure **5e**; exact mass calcd for $C_{17}G_{19}NO_4$ 301.1314, found 301.1329. The picrate salt was prepared for combustion analysis.

Anal. Calcd for $C_{23}H_{22}N_4O_{11}$: C, 52.08; H, 4.18; N, 10.56. Found: C, 52.19; H, 4.12; N, 10.43.

Ethyl 3-carbethoxyquinoline-2-acetate (5f) was prepared from **1a** (1 mmol) and **2f** (121 mg, 1 mmol) by method A. Recrystallization gave pure **5f**, identical in all respects with an authentic sample.[6]

Ethyl 3-carbethoxy-4-hydroxythiophene-2-acetate (5g) was prepared from **1a** (2 mmol) and **2g** (212 mg, 2 mmol) by method B. Column chromatography gave pure **5g**.

Anal. Calcd for $C_{11}H_{14}SO_5$: C, 51.15; H, 5.46; S, 12.42. Found: C, 51.04; H, 5.52; S, 12.51.

Ethyl 3-carbethoxy-4-hydroxy-5-methylthiophene-2-acetate (5h) was prepared from **1a** (4 mmol) and **2h** (448 mg, 4 mmol) by method B. Column chromatography gave pure **5h**.

Anal. Calcd for $C_{12}H_{16}O_5S$: C, 52.93; H, 5.92; S, 11.77. Found: C, 53.02; H, 6.08; S, 11.99.

Ethyl 4-carbethoxy-1,5-diphenylpyrazole-3-acetate (5i) was prepared from **1a** (1 mmol) and **2i** (212 mg, 1 mmol) by method A. Column chromatography gave pure **5i**, identical in all respects with an authentic sample.[7]

Ethyl 4-carbethoxy-5,6-diphenylpyridazine-2-acetate (5j) was prepared from **1a** (1.5 mmol) and **2j** (336 mg, 1.5 mmol) by method A. Column chromatography gave pure **5j**; exact mass calcd for $C_{23}H_{22}N_2O_4$ 390.1577, found 390.1571.

Registry No. **1a**, 52358-42-6; **2a**, 85-91-6; **2b**, 4892-02-8; **2c**, 119-36-8; **2d**, 2835-77-0; **2e**, 551-93-9; **2f**, 529-23-7; **2g**, 2365-48-2; **2h**, 53907-46-3; **2i**, 579-45-3; **2j**, 5344-88-7; **5a**, 73286-07-4; **5b**, 95421-53-7; **5c**, 95421-54-8; **5d**, 17282-92-7; **5e**, 23301-16-8; **5f**, 95421-55-9; **5g**, 95421-56-0; **5h**, 95421-57-1; **5i**, 41470-68-2; **5j**, 95421-58-2.

Supplementary Material Available: IR and NMR spectra of compounds in Table I (1 page). Ordering information is given on any current masthead page.

Epoxidation of Alkenes with Potassium Hydrogen Persulfate

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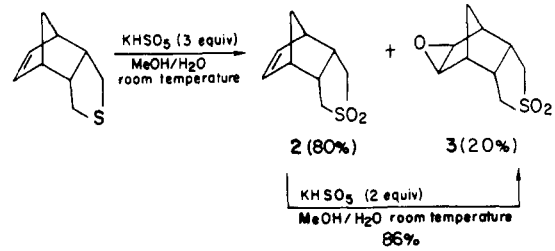
Potassium hydrogen persulfate ($KHSO_5$, potassium caroate), commercially sold as oxone, is a convenient, inexpensive, and powerful oxidant with a wide range of application.[1] It has been recently reported that alkenes[2,3] as well as arenes[4] can be epoxidized by dioxirane intermediates generated in situ by the reaction of potassium hydrogen persulfate with acetone. In the absence of ketones no reaction was observed under the reaction conditions used by the authors. We report now that potassium hydrogen persulfate alone is able to epoxidize water-soluble or insoluble alkenes with good to excellent yields, thus opening a new, efficient, and simple way for epoxide synthesis.

This work was initiated by the fact that in contrast with Trost's report[5] we observed the partial epoxidation of an isolated double bond by $KHSO_5$ in aqueous methanol: up to 20% of epoxide **3** was formed during the reaction of 4-thiatricyclo[5.2.1.$0^{2,6}$]dec-8-ene (**1**) with oxone at room temperature.[6]



When the sulfone **2** was treated with 2 equiv of oxone in the same conditions, a 86% yield of epoxide **3** was obtained after 24 h. These observations led us to examine the epoxidation of various alkenes with potassium hydrogen persulfate in aqueous methanol. The results are summarized in Table I.

In procedure A the reaction medium is acidic (pH 2–3) and only a few epoxides are stable under these conditions (entries 3 and 9). In the other cases this procedure led to products arising from oxirane ring-opening, and epoxidations were best performed by using method B or C where the pH is adjusted to 6 and kept at this value during the whole reaction by controlled addition of an aqueous solution of potassium hydroxide. This pH value was preferred to the one (pH 7.5) used for epoxidation with the caroate/acetone system[2] since the peroxide autodecomposition is much less at pH 6: for example, the yield of 1,2-epoxycycloheptane (**5**) was only 60% when the oxidation was made at pH 7.5 with 2 equiv of $KHSO_5$.

Cyclododecene (entry 4) failed to react with $KHSO_5$ in aqueous methanol, and this result may be due to the lack of solubility of this alkene in the medium. The solubility criterion might account for the differences between the Trost[5] and Curci[2] reports and this work.

No methanol was necessary for the oxidation of a water-soluble olefin like sorbic acid (entry 8). In this particular case the formation of 4,5-epoxy-2-hexenoic acid (**11**) as the unique reaction product is representative of the high selectivity of the oxidation which is confirmed by the lack of reactivity of *trans*-cinnamic acid.

However, the reaction of 4-vinylcyclohexene (entry 5) is not so clean, and we could not avoid the formation of 20% diepoxide even when only 1 equiv of persulfate was used.

Experimental Section

Equipment and Materials. ^1H NMR spectra were measured on Perkin-Elmer R-12A or Perkin-Elmer R-32 spectrometers. IR spectra were run on a Perkin-Elmer 682 instrument. Mass spectra were obtained on a Hewlett-Packard 5992A GC/MS spectrometer. Controlled pH experiments were performed by using a Metrohm

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