Registry No.—1·HCl, 22572-05-0; **2**, 67688-61-3; **2**·HCl, 67688-62-4; **3**, 1068-90-2; **4**, 67688-63-5; **5**, 67688-64-6; **6**, 67688-65-7; **7**, 67688-66-8; **8**, 67688-67-9; **9**, 67737-47-7; **10**, 39254-94-9; **11**, 67688-68-0; 1-chloro-3-methyl-2-butene, 503-60-6; α-toluenethiol, 100-53-8; 1-bromo-3-methylbutane, 107-82-4; ethyl 2-acetamido-2-carbethoxy-5-methylhexanoate, 67688-69-1; 2-acetamido-2-carboxy-5-methylhexanoic acid, 67688-70-4.

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A New Furan Synthesis

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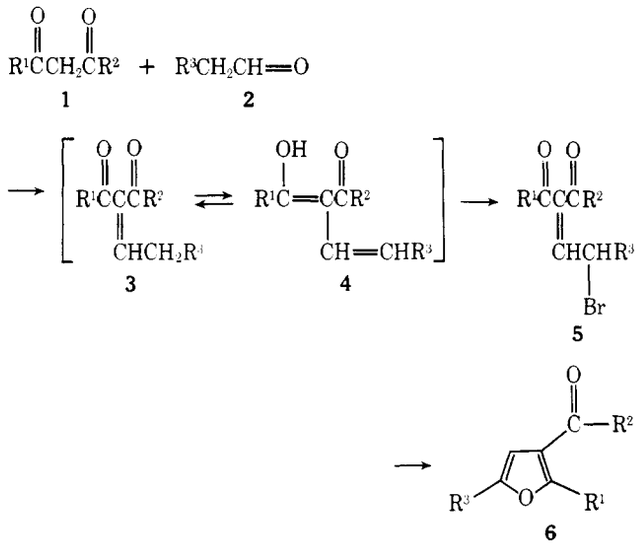
A new furan synthesis is described which comprises reacting an α,β-unsaturated ketone having either an α-carboalkoxy or α-acyl group with *N*-bromosuccinimide and thermally cyclizing the resulting bromine-containing intermediate at a temperature between about 90 and 160 °C. The method is of wide applicability and affords yields in excess of about 70%.

Currently available general methods for the synthesis of furans are essentially limited to the Paal–Knorr synthesis,[2] the condensation of β-keto esters with α-hydroxycarbonyl compounds,[3] and the Feist–Benary method.[4] Unfortunately, these three methods are frequently unsatisfactory. The 1,4-dicarbonyl compounds utilized as starting material in the Paal–Knorr synthesis are often not readily available. Similarly, α-hydroxycarbonyl compounds are frequently unavailable. Finally, the Feist–Benary method requires the use of α-halocarbonyl compounds which are lachrymatory and often not readily available. Although other methods have been reported for the synthesis of furans, these methods appear to be either of relatively limited utility or are inadequately developed.[5]

We now wish to report a new furan synthesis (Scheme I) which is of wide applicability, is simple to carry out, proceeds in high yield, and utilizes readily available starting materials. The required starting material, α,β-unsaturated dicarbonyl compound **3**, is readily available through the Knoevenagel condensation of 1,3-dicarbonyl compound **1** with aldehyde **2**.[6] This α,β-unsaturated compound is not homogeneous, however, and consists of a mixture of geometric isomers in combination with a substantial amount of the corresponding dienol **4**. The Knoevenagel product **3** undergoes an unusually facile allylic bromination upon treatment with an equimolar amount of *N*-bromosuccinimide in carbon tetrachloride at reflux temperature to yield allylic bromide **5**.[7] This material **5**, like its precursor **3**, also consists of a mixture of geometric isomers together with a substantial amount of the corresponding dienol. Carbon tetrachloride is a particularly suitable solvent for this bromination since the succinimide byproduct is relatively insoluble in it and can be easily removed by filtration. The resulting allylic bromide **5** is thermally unstable and undergoes rapid cyclization to yield furan **6** at temperatures in excess of about 80 °C. A variety of substituted furans

Scheme I



were synthesized by this method, and the results are set forth in Table I.

The reaction of **3b** ($R^1 = R^3 = CH_3$; $R^2 = OC_2H_5$) with an equimolar amount of *N*-bromosuccinimide in carbon tetrachloride at reflux temperature (77 °C) was followed by NMR. Under these conditions, the formation of allylic bromide **5b** ($R^1 = R^3 = CH_3$; $R^2 = OC_2H_5$) was complete in approximately 15 min. After 12 h, 60% of the allylic bromide **5b** was converted to ethyl 2,5-dimethyl-3-furoate (**6b**), and after 24 h the only detectable product was furan **6b**. In general, however, such a prolonged reflux period was not utilized to effect cyclization of the intermediate allylic bromide **5**. Since the formation of allylic bromide **5** is very rapid, it was found to be more satisfactory to isolate and distil the crude allylic bromide **5** after

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Table I. Properties and Yields of Intermediates and Furan Products Prepared According to Scheme I

				3[a]		6[a]		
entry	R^1	R^2	R^3	yield, %[b,c]	bp, °C (mm)	yield, %[b,d]	bp, °C (mm)	registry no.
a	CH_3	OC_2H_5	H	56	88–91 (18)[e]	24[f]	87–89 (18)[g]	28921-35-9
b	CH_3	OC_2H_5	CH_3	76	91–93 (12)[h]	83	96–100 (18)[i]	29113-63-1
c	CH_3	OC_2H_5	C_2H_5	63	116–118 (17)[j]	91	99–101 (10)[k]	64354-20-7
d	CH_3	OC_2H_5	$CH(CH_3)_2$	89	110–111 (10)[l]	85	112–114 (11)[m]	3132-66-9
e	CH_3	OC_2H_5	$(CH_2)_4CH_3$	32	104–107 (0.5)[n]	69	115–119 (1.3)	64354-21-8
f	CH_3	OC_2H_5	$(CH_2)_7CH{=}CH_2$	58	135–141 (0.6)	77	147–151 (0.6)	64354-47-8
g	CH_3	OC_2H_5	$(CH_2)_{11}CH_3$	47[o]	155–159 (0.5)	63	160–163 (0.4)	64354-23-0
h	$(CH_2)_2CH_3$	OC_2H_5	CH_3	73	110–113 (12)	85	104–107 (10)	64354-24-1
i	C_6H_5	OC_2H_5	CH_3	64	135–137 (1.4)	92	133–135 (0.6)[p]	29113-65-3
j	CH_3	CH_3	H	50	79–81 (10)[q]	0[r,s]		
k	CH_3	CH_3	CH_3	65	90–92 (20)[t]	66[r]	84–87 (12)[u]	10599-70-9
l	CH_3	CH_3	C_2H_5	49	89–91 (11)[r]	86	84–87 (9)	64354-51-4

[a] All compounds afforded satisfactory NMR and infrared spectra, and satisfactory elemental analyses were obtained for all new compounds. [b] Isolated yield. [c] Except where indicated otherwise, the reaction was carried out without solvent at 5 °C with piperidine as a catalyst and a reaction time of from 18 to 48 h. [d] Except where indicated otherwise, allylic bromination was carried out in CCl_4 under reflux for a period of from 2 to 12 h; after cooling, succinimide was removed by filtration, solvent removed in vacuo, and the crude product distilled in vacuo to yield the furan **6**. [e] Lit.[8] bp 106–110 °C (23 mm). [f] Allylic bromination carried out at reflux for 26 h in a Soxhlet extraction apparatus containing a thimble filled with anhydrous K_2CO_3. [g] Lit.[9] bp 81–84 °C (18 mm). [h] Lit.[8] bp 103–106 °C (11 mm). [i] Lit.[10] bp 99–101 °C (14 mm). [j] Lit.[11] bp 118–120 °C (18 mm). [k] Lit.[12] bp 98–104 °C (11 mm). [l] Lit.[11] bp 120–121 °C (15 mm). [m] Lit.[13] bp 60–65 °C (1 mm). [n] Lit.[8] bp 133–136 °C (8 mm). [o] Reaction carried out at 5 °C for 12 h and then at room temperature for 12 h. [p] Lit.[14] bp 193–194 °C (20 mm). [q] Lit.[15] bp 80–81 °C (10 mm). [r] A 24-h reflux period was utilized. [s] Polymer was isolated. [t] Lit.[16] bp 90–92 °C (19 mm). [u] Lit.[17] 95 °C (23 mm). [r] Lit.[16] 90–92 °C (18 mm).

a 2 to 12 h reaction period in refluxing carbon tetrachloride. At a distillation temperature, in vacuo, of about 90 to 160 °C, cyclization of the allylic bromide **5** was rapid, and the only distillation product isolated was the desired furan **6**. This distillation procedure offers the advantage of a reduced reaction time, and also serves to prevent excessive exposure of the furan product **6** to the hydrogen bromide which is formed as a byproduct during the cyclization of **5**.

The entries in Table I serve to indicate that the yield of furan **6** is generally in excess of about 70%. The versatility of this synthesis is well illustrated by entry **f** in Table I. The α,β-unsaturated dicarbonyl system of **3f** is so highly reactive toward allylic bromination that another isolated double bond survives the reaction conditions unchanged. Consequently, the synthesis set forth in Scheme I permits the direct synthesis of furans which possess substituents containing olefinic unsaturation.

Table I also illustrates one modest limitation of the furan synthesis which is set forth in Scheme I. Entries **a** ($R^1 = CH_3$; $R^2 = OC_2H_5$; $R^3 = H$) and **j** ($R^1 = R^2 = CH_3$; $R^3 = H$) demonstrate that α,β-unsaturated dicarbonyl compounds **3a** and **3j** afford unsatisfactory yields of furans **6a** and **6j**, respectively. The primary cause of this limitation appears to be the fact that furans **6a** and **6j** possess an unsubstituted 5 position on the ring. As a consequence, the hydrogen bromide which is generated through cyclization of the intermediate allylic bromide can either initiate polymerization or add to the furan ring. This problem could be partially controlled, however, by preparing the intermediate allylic bromide **5** in the presence of potassium carbonate. A 24% yield of **6a** was obtained through the use of potassium carbonate in the bromination step, whereas only 13% of **6a** was obtained when potassium carbonate was not used.

A second factor, which may also be responsible for the unsatisfactory yield of furans **6a** and **6j**, is the fact that preparation of the intermediate allylic bromides **5a** and **5j** requires the bromination of a primary allylic carbon atom. In contrast, all other examples set forth in Table I involve the bromination of a secondary allylic carbon atom. It has been demonstrated that a primary allylic position undergoes bromination at a rate which is about two orders of magnitude slower than that for a secondary allylic position.[7b] As a consequence of this slower rate of allylic bromination, substantial amounts of furan product **6** ($R^3 = H$) may be formed in the presence of unreacted *N*-bromosuccinimide. The unconsumed *N*-bromosuccinimide and furan **6** ($R^3 = H$) would be expected to react with each other and result in a loss of both starting material and product.

Experimental Section

All melting points and boiling points are uncorrected. Infrared spectra were determined with a Perkin-Elmer 257 infrared spectrophotometer. NMR spectra were recorded on a Varian T-60 spectrometer with tetramethylsilane as an internal standard. The mass spectra were obtained with a Varian MAT CH7 mass spectrometer. Microanalyses were performed by M-H-W Laboratories, Garden City, Mich. *N*-Bromosuccinimide was freshly recrystallized from water prior to use.[18]

5-Carboethoxy-5-octen-4-one (3h). The following procedure is representative of the general procedure employed for the preparation of the α,β-unsaturated dicarbonyl compounds set forth in Table I.[19] To a mixture of 31.64 g (0.2 mol) of ethyl 3-oxohexanoate and 13.90 g (0.24 mol) of propionaldehyde at ice-bath temperature was added a solution of 0.2 g of piperidine in 0.4 g of absolute ethanol with magnetic stirring. The reaction mixture was then allowed to stand at 5 °C in the refrigerator for 36 h. The resulting mixture was diluted with 75 mL of ether and washed three times with 40-mL portions of half-saturated brine which contained a few drops of acetic acid. The combined aqueous washes were extracted twice with 40-mL portions of ether. The combined organic layers were washed once with 40 mL of saturated brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo to give 36.0 g of crude product. Fractional distillation through a 10-cm Vigreux column then afforded 28.4 g (73%) of 5-carboethoxy-5-octen-4-one (**3h**): bp 110–113 °C (12 mm); IR (neat) 1715 (C=O) and 1638 cm^{-1} (C=C); NMR (CCl_4) δ 7.15 (0.29 H, t, $J = 8$ Hz, C=C**H**CH_2, *Z* isomer), 7.08 (0.29 H, t, $J = 8$ Hz, C=C**H**CH_2, *E* isomer), 5.73–6.37 (0.84 H, m, C**CH**=**CH**CH_3, dienol); mass spectrum (70 eV) *m/e* 198 (M^+). Redistillation afforded the analytical sample: bp 112 °C (13 mm).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.73; H, 8.96.

Ethyl 5-Methyl-2-propyl-3-furoate (6h). The following procedure is representative of the general procedure employed for the preparation of the furans set forth in Table I. To a slurry of 3.560 g (20 mmol) of *N*-bromosuccinimide in 40 mL of carbon tetrachloride was added a solution of 3.969 g (20 mmol) of 5-carboethoxy-5-octen-4-one (**3h**) in 10 mL of carbon tetrachloride. The resulting mixture was then heated at reflux for 12 h. After cooling the resulting mixture, the insoluble succinimide byproduct was removed by filtration and

the filtrate concentrated in vacuo to give 5.0 g of crude product. Short-path distillation afforded 3.35 g (85%) of furan **6h:** bp 104–107 °C (10 mm); IR (neat) 1711 (ester C=O) and 1538 cm^{-1} (furan); NMR (CCl_4) δ 6.47 (1 H, s, furan **H**), 4.53 (2 H, q, J = 8 Hz, OCH_2CH_3), 3.05 (2 H, t, J = 8 Hz, CCH_2CH_2), 2.37 (3 H, s, CCH_3), 1.56–2.07 (2 H, m, $CH_2CH_2CH_3$), 1.38 (3 H, t, J = 8 Hz, OCH_2CH_3), 1.00 (3 H, t, J = 8 Hz, CH_2CH_3); mass spectrum (70 eV) m/e 196 (M^+). Redistillation afforded the analytical sample: bp 106.5 °C (11.5 mm).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.13; H, 8.09.

Ethyl 2-Methyl-3-furoate (6a). A. Preparation in the Absence of K_2CO_3. A solution of 3.124 g (20 mmol) of ethyl 2-acetyl-2-butenoate (**3a**) in 10 mL of carbon tetrachloride was added to a suspension of 3.559 g (20 mmol) of *N*-bromosuccinimide in 40 mL of carbon tetrachloride, and the resulting mixture was heated at reflux for 19 h. After cooling to room temperature, the insoluble succinimide byproduct was removed by filtration. Concentration of the filtrate in vacuo followed by short-path distillation afforded 0.4 g (13%) of **6a:** bp 87–89 °C (18 mm) [lit.[9] bp 81–84 °C (18 mm)]. A second fraction from the distillation was tentatively identified as ethyl 5-bromo-2-methyl-3-furoate, apparently formed by bromination of **6a:** bp 110–114 °C (20 mm); NMR (CCl_4) δ 6.88 (1 H, s, furan **H**), 4.46 (2 H, q, J = 8 Hz, OCH_2CH_3), 2.71 (3 H, s, CCH_3), and 1.39 (3 H, t, J = 8 Hz, OCH_2CH_3).

B. Preparation of 6a in the Presence of K_2CO_3. The reaction, as set forth above under **A**, was repeated using a Soxhlet extraction apparatus which contained a thimble loaded with 5.52 g (40 mmol) of anhydrous K_2CO_3. The reaction mixture was heated at reflux for 26 h during which the initially red mixture became pale yellow and the thimble became black. The resulting reaction mixture was workedup as described above under **A** to afford 0.73 g (24%) of furan **6a.**

Ethyl 2-Acetyl-4-bromo-2-pentenoate (5b). A mixture of 8.06 g (47 mmol) of ethyl 2-acetyl-2-pentenoate and 8.43 g (47 mmol) of *N*-bromosuccinimide in 50 mL of carbon tetrachloride was heated at reflux for 15 min. The mixture was then quickly cooled to room temperature, and the succinimide byproduct removed by filtration. Concentration of the filtrate in vacuo afforded 11.5 g (98%) of crude ethyl 2-acetyl-4-bromo-2-pentenoate (**5b**): NMR (CCl_4) δ 7.30 (0.44 H, d, J = 6 Hz, C=C**H**CHBr, *Z* isomer), 7.11 (0.47 H, d, J = 6 Hz, C=C**H**CHBr, *E* isomer), 6.63 (0.09H, s, CC**H**=CBr, dienol).

Registry No.—**1a,** 141-97-9; **1h,** 3249-68-1; **1i,** 94-02-0; **1j,** 123-54-6; **2a,** 75-07-0; **2b,** 123-38-6; **2c,** 123-72-8; **2d,** 78-84-2; **2e,** 111-71-7; **2f,** 112-45-8; **2g,** 124-25-4; (*Z*)-**3a,** 67556-07-4; (*E*)-**3a,** 67556-08-5; (*Z*)-**3b,** 67556-09-6; (*E*)-**3b,** 67556-10-9; (*Z*)-**3c,** 15802-68-3; (*E*)-**3c,** 15802-67-2; (*Z*)-**3d,** 67556-11-0; (*E*)-**3d,** 67556-12-1; (*Z*)-**3e,** 67556-13-2; (*E*)-**3e,** 67556-14-3; (*Z*)-**3f,** 67556-15-4; (*E*)-**3f,** 67556-16-5; (*Z*)-**3g,** 67556-17-6; (*E*)-**3g,** 67556-18-7; (*Z*)-**3h,** 67556-19-8; (*E*)-**3h,** 67556-20-1; (*Z*)-**3i,** 39626-67-0; (*E*)-**3i,** 39626-68-1; (*Z*)-**3j,** 67556-21-2; (*E*)-**3j,** 67556-22-3; (*Z*)-**3k,** 67556-23-4; (*E*)-**3k,** 67556-24-5; (*Z*)-**3l,** 67556-25-6; (*E*)-**3l,** 67556-26-7; (*Z*)-**5b,** 67556-27-8; (*E*)-**5b,** 67556-28-9; ethyl 5-bromo-2-methyl-3-furoate, 35304-35-9.

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Synthetic Studies toward Complex Diterpenoids. 10.[1] Stereocontrolled Total Synthesis of (±)-19α,20α-(Acetylimino)-12-hydroxy-5β,10α-podocarpa-8,11,13-triene, a Degradation Product of Atisine

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A stereocontrolled total synthesis of (±)-19α,20α-(acetylimino)-12-hydroxy-5β,10α-podocarpa-8,11,13-triene (**10**) through the tetracyclic ketone **11** and the dicarboxylic acid **28** is reported. The synthetic approach utilizes two stereoselective methods of angular alkylations. The first one is based upon a regioselective intramolecular α-oxocarbenoid insertion across the benzylic C–H (at C-10) bond in the copper-catalyzed carbenoid decomposition of α-diazomethyl ketone **23,** prepared from the tricyclic acid **22.** The second route consists of a stereospecific rearrangement of cyclobutanone **26,** easily accessible from the β,γ-unsaturated tricyclic acid **18** via the corresponding α-diazomethyl ketone **24** and the unsaturated cyclobutanone **25.** The starting tricyclic acids have been prepared by two alternate routes from Hagemann's ester (**12**) and 7-methoxy-1-tetralone (**19**).

The tetracyclic amines, such as **1** and **2,** are key intermediates in a number of total syntheses[2] of *Garrya* and *Atisine* groups of diterpene alkaloids. Any useful synthesis[1-3] of these compounds requires both stereochemical control of the C-1 and C-4a substituents in a *trans*-hydrophenanthrene moiety and an appropriate oxygen functionality in the aromatic ring for further elaborations. In our earlier papers[1,4] we reported two simple stereocontrolled synthetic approaches to the tetracyclic ketones **6** and **7** and illustrated their versatility[1] by total synthesis of the tetracyclic acetylamines **8** and **9.** We wish to report herein the details of the first stereocontrolled total synthesis of (±)-19α,20α-(acetylimino)-12-hydroxy-5β,10α-podocarpa-8,11,13-triene (**10**), a major degradation product[5] of atisine and a potential intermediate[6] toward the

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