Tetrahedron Vol. 46, No. 12, pp. 4407–4416, 1990
Printed in Great Britain

0040-4020/90 $3.00+.00

REACTION OF METHYL 2,3-PENTADIENOATE WITH BROMINE. PREPARATION OF 4-BROMO-5-METHYL-5H-FURAN-2-ONE.

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(*Received in UK 6 April* 1990)

Abstract.- Treatment of methyl 2,3-pentadienoate, **3**, with bromine in carbon tetrachloride affords a complex mixture, whose main products are methyl (E)- and (Z)-3,4-dibromo-2-pentenoate, **9** and **10**, and 4-bromo-5-methyl-5H-furan-2-one, **4**. The mechanism of formation of these and other minor compounds is discussed. Hydrolysis of the crude mixture in the presence of barium hydroxide affords lactone **4** in 30% overall yield.

INTRODUCTION

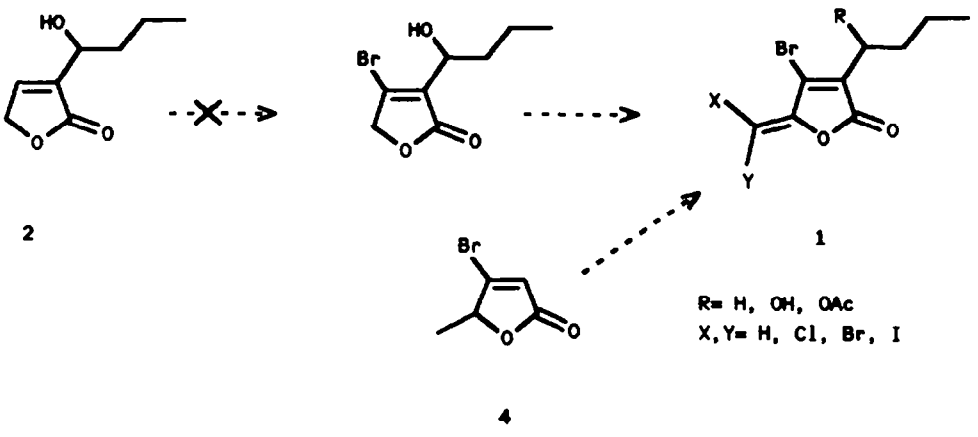
Fimbrolides, **1**, isolated from the red marine algae Delisea fimbriata, are halogenated butenolides with interesting antifungal and antimicrobial properties.[1] Several attempts to synthesise these novel secondary metabolites have been described, but until now very little success has been achieved.[2]

One of the problems in the synthesis of these molecules is the introduction of the bromine atom at the β-position of the butenolide. We have recently shown that the incorporation of bromine into 3-(1-hydroxybutyl)-5H-furan-2-one, **2**, by bromination and dehydrobromination failed, because this butenolide did not add bromine giving rise instead to the substitution of the hydroxyl group by halogen[3] (Scheme 1). Therefore, new synthetic approaches to β-bromobutenolides were needed. In this work we present a study on the transformation of allenic esters into β-bromobutenolides, a reaction already described[4], but that with our substrate (methyl 2,3-pentadienoate, **3**) resulted to be rather complex, allowing us to isolate some new products and to investigate its mechanism.

REACTION OF METHYL 2,3-PENTADIENOATE 3 WITH BROMINE

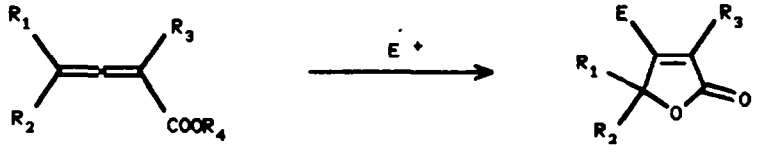
We visualized 4-bromo-5-methyl-5H-furan-2-one, **4**, as a key intermediate in a new synthetic approach to fimbrolides **1**. Compound **4** has been only described by E. Shaw,[5] who isolated it in very low yield and without fully characterization from a complex reaction mixture obtained from the successive reactions of 3-bromolevulinic acid with acetic anhydride and anhydrous sodium acetate.

Other general approaches to β-bromobutenolides already described in the literature are: i) treatment of the diethyl acetal of 3-bromo-3-lithioacrolein[6] or the not easily



SCHEME 1

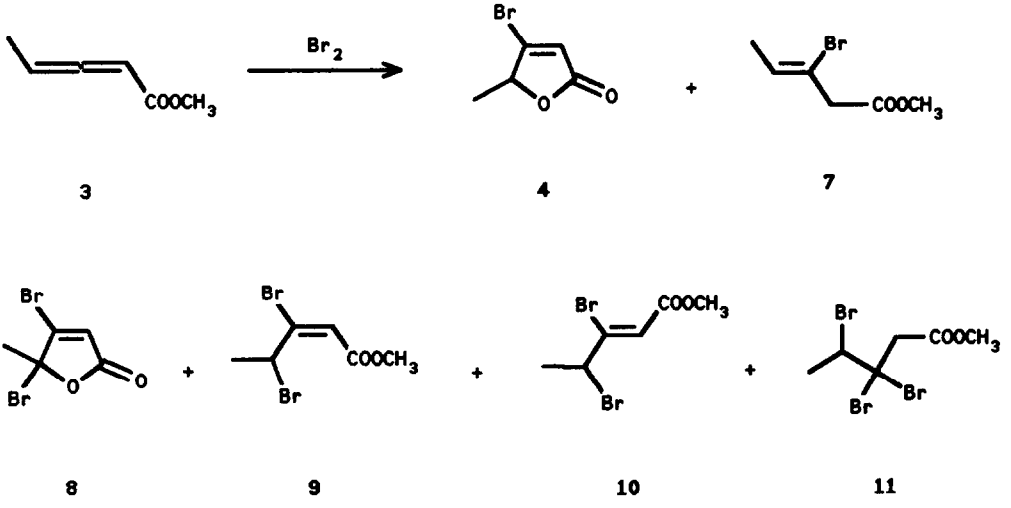
available lithium (E)-2-alkyl-3-bromo-3-lithiopropenoates[7] with aldehydes; ii) the bromination-dehydrobromination of γ-alkoxybutenolides[8]; and iii) reaction of bromine with the readily accessible allenic acids or esters, 5 (Scheme 2).[4] The first method has been successfully applied recently to a synthesis of a fimbrolide[9] (1, R=X=H, Y=Br); the second one requires the presence of an alkoxy group at the γ-position; therefore we focused our attention on the third reaction. This electrophilic initiated cyclization of allenic acids and esters is a general route for the synthesis of β-substituted-α,β-unsaturated butenolides, 6. Nevertheless, reaction with bromine is described only with satisfactory yields for R^1=Ph, R^2=H, alkyl[4a,b] or R^1 and R^2=alkyl.[4c,d]



5 6

SCHEME 2

When methyl 2,3-pentadienoate, 3,[10] was submitted to the conventional ionic bromination conditions (1 equivalent of bromine in carbon tetrachloride at room temperature) a very complex mixture, containing mono-, di-, tri-, and tetrabromo derivatives was obtained (Scheme 3). The reaction was repeated under different concentration conditions and with defect or excess of bromine, but the final results, after analysis by gas chromatography on a capillary column, did not differ considerably (Table 1). Column chromatography of the crudes allowed the isolation of compounds 4, 7, 8, 9, 10, and 11, whose constitutions were assigned by their spectroscopic characteristics. The presence of other tri- and tetrabromo derivatives could be established by their mass spectra obtained by gc-ms analyses. The most remarkable feature of this reaction is that the desired compound 4 is formed only to a small extent, while the main product results from the bromine addition to the non-conjugated double bond giving rise to methyl (E)- and (Z)-3,4-dibromo-2-pentenoate isomers, 9 and 10.



SCHEME 3

Table 1. Bromination reactions of methyl 2,3-pentadienoate, 3.[a]

		4	7	8	9	10	11	12	13
1 M Conc.	0.7 eq. Br_2	11	13	5	41	15	4	2	-
	1 eq. Br_2	15	-	5	52	8	8	2	3
	1.2 eq. Br_2	9	-	8	46	10	16	3	2
0.1 M Conc.	0.8 eq. Br_2	4	4	3	60	13	3	1	-
	1 eq. Br_2	2	1	-	56(53)[b]	11(8)[b]	5	7	4

[a] Composition of the crude mixture determined by gas chromatography (% given; values not corrected for FID response factors). Compounds 7-11 are numbered following the elution sequence in gc. Other minor peaks are present.
[b] Isolated yield.

Pmr spectrum of lactone 4 showed no signal in the region δ 3.5-3.8 indicating the absence of a methoxy group, but a quartet at δ 5.06, showing the butenolide formation; its mass spectrum presented a molecular ion at m/e=178-176 $(C_5H_5BrO_2)^+$, and its ir spectrum had an absorption at 1744 cm^{-1}, in accordance with the presence of an α,β-unsaturated five membered lactone.

The new compound methyl 3-bromo-3-pentenoate, 7, was an oil whose mass spectrum presented a molecular ion at m/e=194-192, that revealed the incorporation of hydrogen bromide to the starting material 3. Addition of HBr has taken place at the conjugated double bond as clearly demonstrated by the line broadened pmr spectrum of 7, that showed, among other signals, a triplet quartet at δ 5.91 (J=6.5 Hz, J'=1.0 Hz) and a doublet triplet at δ 1.77 (J=6.5 Hz, J'=1.1 Hz). The observation of these triplets was coherent with the presence of a methylene group at the C-2 position. These methylenic protons absorb at δ 3.48, a value consistent with the previously observed chemical shift (δ 3.42) of the methylene group of ethyl 3-bromo-3-butenoate.[11] The olefinic proton (δ 5.9) presented a nuclear Overhauser effect (20%) from the methylene group, thus establishing the (Z)-configuration of the double bond.

The structural assignment of 4,5-dibromo-5-methyl-5H-furan-2-one, 8, was unambiguous since the ir spectrum presented an absorption at 1764 cm^{-1}, the pmr spectrum showed only two singlets at δ 2.16 and 6.33, and the chemical ionization mass spectrum had signals at m/e=276-274-272 corresponding to the ion $(C_5H_4Br_2O_2+18)^+$.

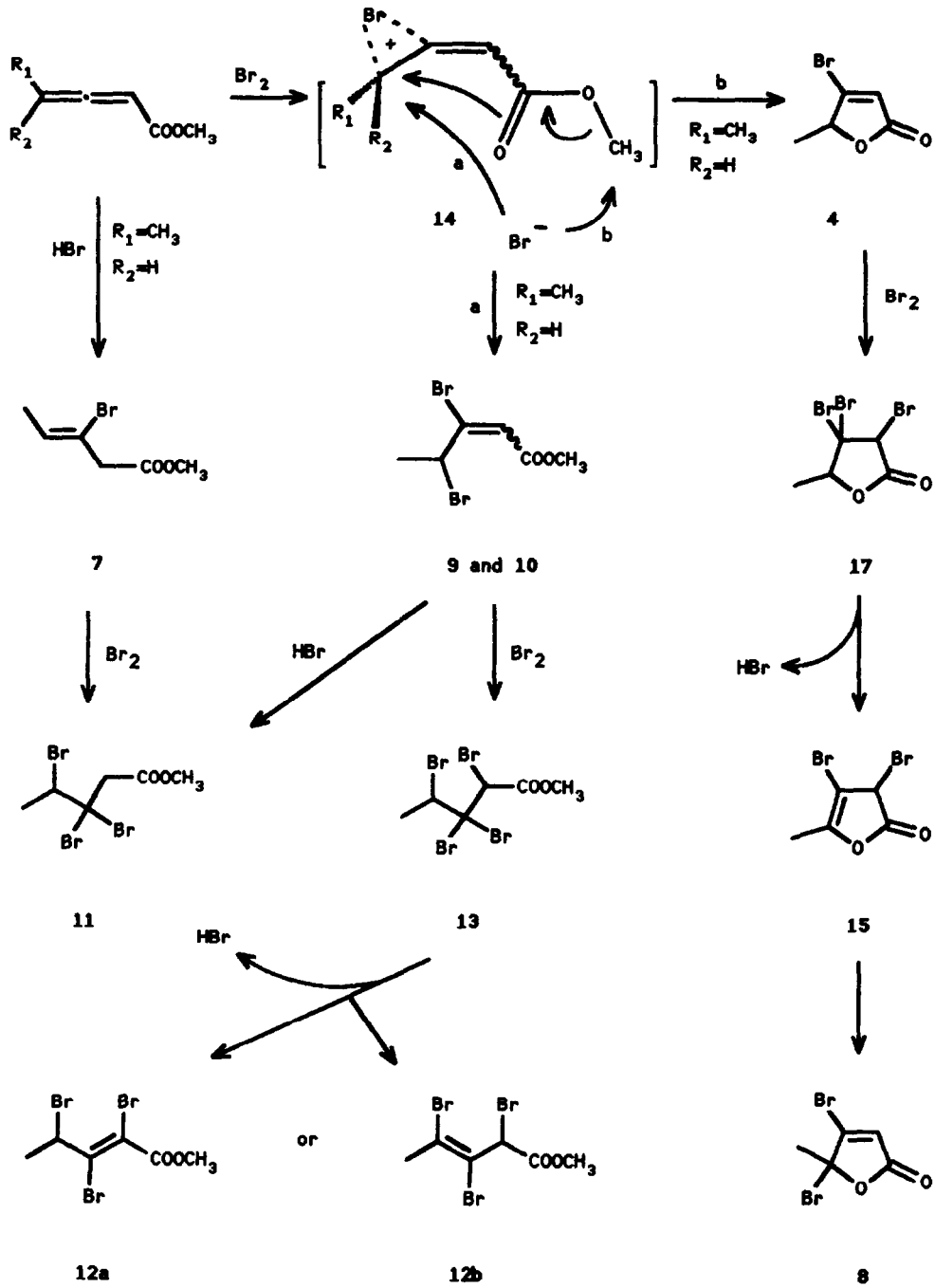
Methyl 3,4-dibromo-2-pentenoates, 9 and 10, are the major compounds in all the experiments. The ir spectra of both compounds presented absorptions at 1710 and 1720 cm^{-1} respectively, in accordance with the presence of a conjugated carboxylate group. Isomer 10 showed in its pmr spectrum a quartet at δ 4.82 ppm, while 9 had this signal strongly deshielded at δ 6.42 ppm; this proves[12] the cis-relationship between the bromomethine group and the ester group in compound 9. This stereochemical assignment is confirmed by the absorptions of C-3 at 149.7 and 141.0 ppm in the cmr spectra of 9 and 10 respectively.[13] Therefore, the main isolated compound in the reaction of 3 with bromine is methyl (E)-3,4-dibromo-2-pentenoate, 9.

The pmr spectrum of methyl 3,3,4-tribromopentanoate, 11, showed an AB system centered at δ 3.88 due to the diastereotopic protons of the methylene group. Its mass spectrum presented signals at m/e=325-323-321-319 corresponding to the elimination of the methoxy group from the molecular ion.

Gas chromatographic analysis indicated other minor components with higher retention times. Two of these signals are tentatively assigned to methyl 2,3,4-tribromo-2-pentenoate, 12a, or its non-conjugated isomer, 12b, and to methyl 2,3,3,4-tetrabromopentanoate, 13, based on their mass spectra (Scheme 4).

MECHANISTIC CONSIDERATIONS

Our results indicate that allene 3 gives competitively addition and cyclization



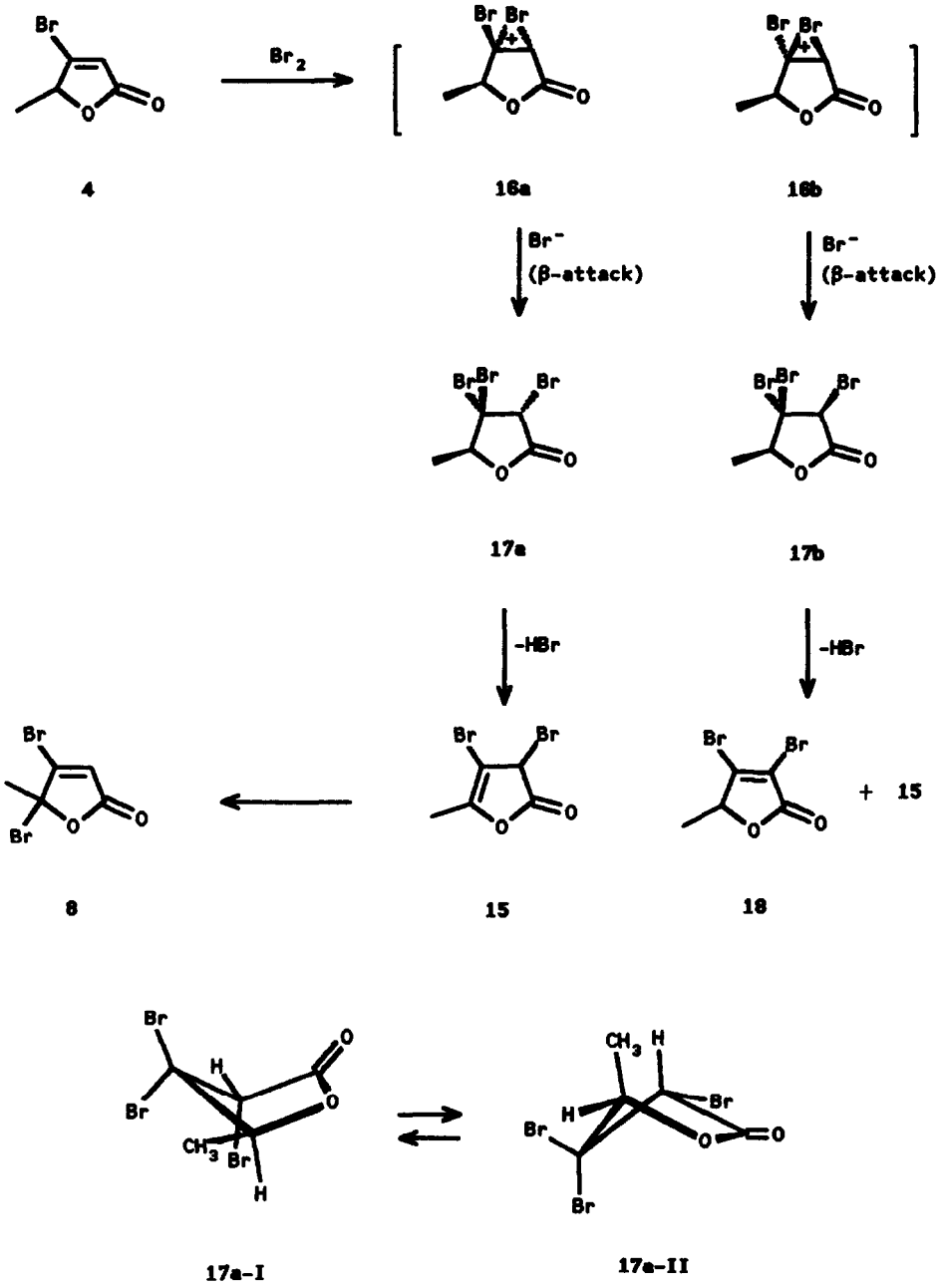
SCHEME 4

reactions under ionic bromination conditions. This behaviour contrasts with the reaction mentioned above between bromine and 4,4-disubstituted allenic esters 5, that affords exclusively β-bromolactones in very good yields. On the other hand, R. Vessière and co-workers[14] described the formation of complex mixtures in the reaction of ethyl 2,3-butadienoate, a non-substituted allenic ester, with bromine: products derived from halogen or hydrogen halide addition to the double bonds but no bromolactones were identified. All these findings can be rationalized from the different charge distribution on the atoms of the unsymmetrical bromonium ion 14. If $R^1=R^2=H$, very little positive charge density resides on C-4.[15] Pathway a, i.e. nucleophilic attack of bromide ion, is thus favoured due to the lack of steric hindrance and the poor carbonyl nucleophilicity. But if the positive charge density on C-4 is stabilized by inductive ($R^1=R^2=$alkyl)[4c,d] or resonance effects ($R^1=$aryl, $R^2=H$, alkyl)[4a,b] an intramolecular attack is preferred and the reaction follows pathway b with the formation of the lactone ring. With our allene 3 both reaction pathways can occur simultaneously, although pathway a dominates giving rise to compounds 9 and 10 as the major products. Moreover, the main product in our bromination reactions, the (E)-isomer 9, derives from the electrophilic attack of bromine to the less hindered side of the allene, anti to the ester group. A second bromination of these derivatives should give 13, that by dehydrobromination should account for the presence of 12a and/or 12b.

Lactone 8 comes from 4 as an independent bromination experiment of this monobromolactone showed. Indeed, reaction of 4 in the darkness with an equivalent of bromine gave 8 in 63% of isolated yield. For the formation of the dibromolactone 8 from 4 we postulate the β,γ-unsaturated lactone 15 as intermediate, that at hand derives from bromonium ion **16a** (Scheme 5). The electrophilic attack of bromine to 4 can afford bromonium ions **16a** or **16b**. Assuming a kinetic control of this reaction, the anti attack from the less hindered side of the lactone ring should predominate. Since bromide ion nucleophilic attack must be produced at the β-position according to the work of Heasley[16] and Pitkanen,[17] tribromolactone **17a** is the most likely bromine adduct formed, instead of **17b**. A MNDO calculation gave **17a-I** as the more populated conformer, being 0.98 kcal x mol^{-1} more stable than **17a-II**. With the methyl group in pseudo-equatorial position and only one bromine-bromine gauche interaction **17a-I** can perform easily a hydrogen bromide elimination to form the non-conjugated dibromolactone 15. Bromine allylic rearrangement should account for the final conjugated lactone 8. A similar transposition has been recently described in a six membered lactone.[18] On the other hand, if **17b** was the initial step of the mechanistic pathway, 18 should be mainly formed in addition to 15 (i.e. 8). That product has never been detected.

Compound 7 should result from the hydrogen bromide addition to the conjugate double bond of the starting allene 3. Hydrogen bromide is always formed in these reactions with bromine and Vessière[14] already observed hydrogen halide additions in the halogenations of allenes. As a matter of fact independent reaction of 3 with hydrogen bromide resulted in the isolation of 7 in a 83% yield.

Finally, compound 11 should result from the double addition of bromine and hydrogen bromide to allene 3.


Br
Br2
Br Br
4
16a
16b
Br-
(β-attack)
Br-
(β-attack)
17a
17b
-HBr
-HBr
+ 15
8
15
18
CH3
H
17a-I
17a-II

SCHEME 5

PREPARATION OF 4-BROMO-5-METHYL-5H-FURAN-2-ONA, 4

We have done several attempts to convert the main compound **9** into the desired lactone **4** by saponification and lactonization of the corresponding hydroxy acid. The best results were obtained when the crude reaction mixture derived from the bromination of **3** was treated directly with a 0.15 M solution of barium hydroxide. Under these conditions we were able to isolate **4** in a 30% overall yield.

In conclusion, we have identified most of the products resulting from the bromination of methyl 2,3-pentadienoate and we describe herein a new synthesis of 4-bromo-5-methyl-5H-furan-2-one. The application of this reaction to other appropriate substrates for the synthesis of fimbrolides is under study in our laboratories.

EXPERIMENTAL SECTION

Melting points have been determined on a Kofler hot stage and are uncorrected. Uv and ir spectra were recorded on a Hewlett-Packard 8452A and a Nicolet ZDX spectrophotometers respectively. The 80 MHz pmr and 20 MHz cmr spectra were recorded on a Bruker WP80SY spectrometer from deuterated chloroform solutions; chemical shifts are given in ppm relative to TMS (δ values). Distillation of small amounts were effected on a Büchi KRV 65/30 rotational distillator (only oven temperature given). Gas chromatographic analyses were performed on a Hewlett-Packard model 5930 instrument with a capillary column Hewlett-Packard Ultra 1 (crosslinked methyl silicone gum, 12m x 0.2 mm x 0.3 µm; injector and detector: 210°C; T_1: 60°C; t_1: 3 min; T_2: 80°C with a rate of 5°C/min; T_3: 200°C with a rate of 10°C/min. Mass spectra and gc-ms analyses (70 eV for electron impact, and ammonia as reagent gas for chemical ionization) were recorded on a Hewlett-Packard 5985B gc-ms system with the previously described capillary column.

Methyl 2,3-pentadienoate, **3**.

This product was prepared following the method of R.W. Lang[10b] by the reaction between propionyl chloride and commercial methoxycarbonylmethylentriphenylphosphorane.

General bromination reaction. Isolation and purification of compounds **4**, **7**, **8**, **9**, **10**, and **11**.

To a stirred solution of 1.013 g (9.03 mmols) of allene **3** in carbon tetrachloride (9 mL) 0.7 mL of a 9 M solution of bromine in CCl_4 (6.3 mmols) were slowly added at room temperature. When the addition was finished the crude mixture was washed successively with a 0.5 M solution of sodium bisulphite and water. The resulting solutions obtained using different allene concentrations and bromine equivalents (Table 1) were analysed by gc.

A crude mixture of 2.76 g arising from several brominating experiments was chromatographed through a silica gel column (230-400 mesh) affording the following fractions:

i) With hexane-ether (19:1) as eluent 1.258 g of a mixture of **9** and **11**. This fraction was submitted to two distillations. The head of the second operation (94 mg, b.p. 43-55°C/0.3 torr) was a colorless liquid identified as **9**. The residue was again chromatographed on silica gel with hexane as eluent affording, among others, a fraction (32 mg) of **11** as a yellow oil.

ii) With hexane-ether (9:1) as eluent 776 mg of a mixture containing **7**, **8**, and **10**. This mixture was distilled yielding three fractions of b.p. 20-30°C, 30-36°C, and 36-45°C at 0.2 torr. A new distillation of the first fraction afforded **7** (62 mg, b.p. 49-53°C/10 torr). The addition of pentane to the second fraction yielded white crystalls identified as **8** (60 mg, m.p. 88-90°C). Distillation and column chromatography of the third fraction allowed the isolation of pure **10** (72 mg), oil.

iii) With hexane-ether (1:1) as eluent 190 mg of a white solid identified as **4**. Recrystallization of this solid in pentane yielded pure **4** (m.p. 52-53°C, lit.[5] 51-53°C).

Spectroscopic data:

4: ir (KBr) 3113, 2994, 1744, 1599, 1255, 1163, 932, 869 cm^{-1}; uv (methanol) 224 nm ($\log \varepsilon$=4.1); pmr 1.57 (d, J=6.8 Hz, 3H), 5.06 (dq, J=6.8 Hz, J'=1.6 Hz, 1H), 6.30 (d, J=1.6 Hz, 1H); cmr 18.2, 81.9, 121.6, 151.8, 169.8; ms, m/e 178-176 (M^+, 5, 6), 163 (31), 161 (32), 135 (13), 133 (10), 97 (100), 53 (21), 43 (24). Anal. Calcd. for $C_5H_5BrO_2$: C, 33.93; H, 2.85; Br, 45.15. Found: C, 33.86; H, 2.79; Br, 45.16.

7: ir (neat) 2956, 1746, 1663, 1436, 1340, 1262, 1171 cm^{-1}; pmr 1.77 (dt, J=6.5 Hz, J'=1.1 Hz, 3H), 3.48 (m, 2H), 3.72 (s, 3H), 5.91 (tq, J=6.5 Hz, J'=1.0 Hz, 1H); cmr 17.0, 46.6, 52.0, 118.8, 128.3, 170.0; ms m/e 194-192 (M^+, 21, 20), 163 (5), 161 (6), 135 (22), 133 (26), 113 (100), 59 (37), 53 (62). Anal. Calcd. for $C_6H_9BrO_2$: C, 37.32; H, 4.70. Found: C, 36.80; H, 4.69.

8: ir (KBr) 3125, 1789, 1764, 1597, 1233, 1075, 930 cm^{-1}; uv (chloroform) 242 nm ($\log \varepsilon$=3.9); pmr 2.16 (s, 3H), 6.33 (s, 1H); cmr 30.1, 92.2, 120.7, 154.7, 166.0; ms m/e 215-213-211 (M^+-43, 0.5, 1.9, 1.0), 177 (100), 175 (100), 135 (28), 133 (30); ms (CI/NH_3) 276-274-272 (M^+ + 18). Anal. Calcd. for $C_5H_4Br_2O_2$: C, 23.47; H, 1.58. Found: C, 23.87; H, 1.42.

9: ir (neat) 2935, 1710, 1605, 1424, 1337, 1200, 1176, 1104 cm^{-1}; uv (methanol) 241 nm; pmr 1.82 (d, J=6.6 Hz, 3H), 3.78 (s, 3H), 6.33 (s, 1H), 6.42 (q, J=6.6 Hz, 1H); cmr 25.2, 43.3, 52.0, 123.0, 149.7, 164.0; ms m/e 274-272-270 (M^+, 2, 4, 2), 243 (5), 241 (10), 239 (5), 215 (4), 213 (9), 211 (5), 193 (85), 191 (100), 165 (32), 163 (33), 112 (22). Anal. Calcd. for $C_6H_8Br_2O_2$: C, 26.50; H, 2.96. Found: C, 26.60; H, 2.98.

10: ir (neat) 2933, 1720, 1612, 1423, 1271, 1189, 1010 cm^{-1}; uv (methanol) 237 nm; pmr 1.90 (d, J=6.7 Hz, 3H), 3.79 (s, 3H), 4.82 (q, J=6.7 Hz, 1H), 6.67 (s, 1H); cmr 25.2, 51.0, 51.8, 120.3, 141.0, 164.1; ms m/e 274-272-270 (M^+, 2, 4, 2), 243 (8), 241 (15), 239 (8), 215 (8), 213 (16), 211 (9), 193 (100), 191 (100), 165 (36), 163 (40), 112 (38), 81 (21), 59 (37), 53 (47), 51 (22).

11: pmr 2.05 (d, J=6.6 Hz, 3H), 3.74 (s, 3H), 3.76 (d, J=17.2 Hz, 1H), 4.00 (d, J=17.2 Hz, 1H), 5.21 (q, J=6.6 Hz, 1H); ms m/e 325-323-321-319 (M^+-31, 0.1, 0.5, 0.8, 0.1), 275 (15), 273 (31), 271 (16), 193 (24), 191 (27), 133 (27), 59 (55), 53 (100).

12: ms m/e 339-337-335-333 (M^+-15, 0.1, 0.3, 0.3, 0.1), 273 (2), 271 (5), 269 (2), 247 (8), 245 (13), 243 (6), 59 (11), 43 (100).

13: ms m/e 405-403-401-399-397 (M^+-31, 0.2, 2, 3, 1, 0.2), 355 (22), 353 (69), 351 (52), 349 (25), 273 (43), 271 (100), 269 (51), 215 (20), 213 (3), 211 (20), 40 (13).

Reaction of allene **3** with hydrogen bromide in acetic acid.

A solution of 175 mg (1.56 mmol) of **3** in carbon tetrachloride (12 mL) was placed in a septum stopped flask. Then 0.32 mL (1.82mmol) of a 33% solution of HBr in acetic acid were slowly added through a mycrosyringe at room temperature and under stirring. The resulting mixture was immediately diluted with methylene chloride (10 mL) and was washed succesively with $NaHCO_3$ solution and water. The organic phase was dried over anhydrous sodium sulphate and the solvent was eliminated under reduced pressure to yield 296 mg of a yellow oil. Distillation of this oil afforded 249 mg of **7** (83% yield, b.p. 50-53°C/10 torr).

Reaction of lactone **4** with bromine.

To a light protected and magnetically stirred solution of lactone **4** (77 mg, 0.44 mmol) in carbon tetrachloride (0.5 mL) were added 0.2 mL of a 2.17 M solution of bromine in CCl_4 (0.43 mmol) at room temperature. The mixture was stirred at 20°C for 16 h and the solvent was eliminated under reduced pressure to afford a yellow oil (110 mg), which was chromatographed on a silica gel column. Elution with hexane-ether (9:1) afforded 62 mg (63% yield) of 4,5-dibromo-5-methyl-5H-furan-2-one, **8**, and 9 mg (12% yield) of starting material. Elution with hexane-ether (1:1) afforded a colorless oil[19] (17 mg, 23% yield), that was identified as 3-bromolevulinic acid by its ir and pmr spectra.

Preparation of 4-bromo-5-methyl-5H-furan-2-one, **4**.

To a magnetically stirred solution of allene **3** (1.21 g, 11 mmol) in carbon tetrachloride (80 mL) at 0°C, a solution of bromine (1.56 g, 10 mmol) in the same solvent was slowly added during 4.5 h. The solution was kept at room temperature for 15 h. The resulting mixture was washed with a 0.5 M solution of $NaHSO_3$ (50 mL) and water (50 mL). The organic phase was dried over anhydrous sodium sulphate and the solvent was eliminated under

reduced pressure at 20°C affording a yellow oily residue (2.35 g), whose gc analysis indicated mainly the presence of compounds **9** (59%) and **10** (12%).

A solution of barium hydroxide octahydrated (3.47 g, 11 mmol) in water (80 mL) was added to the previously obtained crude and the mixture was stirred at room temperature for 18 h. This emulsion was acidified with 2 N HCl to pH 1-2 and was continuously extracted with chloroform (100 mL) during 20 h. The organic phase was dried over anhydrous sodium sulphate and the solvent was eliminated under reduced pressure at 20°C affording 933 mg of an oily residue that was purified by flash column chromatography on silica gel using hexane-ether mixtures as eluent. This purification allowed the isolation of 572 mg (30% overall yield) of pure lactone **4**.

Acknowledgments.- We gratefully acknowledge the "Ministerio de Educación y Ciencia" for financial support through "Dirección General de Investigación Científica y Técnica" (project PB86-0320) and for a grant (A.G.). We also thank Dr. C. Jaime for helpful discussions on MNDO calculations.

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