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Synthesis of 3,4,7,8-tetraalkyl-2-oxa-bicyclo[4.2.0]octa-1(6),3,7-trien-5-ones (**4a-d**), 4,5,7,8-tetraalkyl-2-oxa-bicyclo[4.2.0]octa-1(6),4,7-trien-3-ones (**6a-d**) and 3,4,7,8-tetraalkyl-2*H*,5*H*-cyclobuta[*b*]pyrano-[2,3-*d*]pyran-2,5-diones (**7a-d**) from the reaction of alkynes (**1a-d**) with carbon suboxide (**2**) in various molar ratios is described.

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The reactions of carbon suboxide with different substrates have been extensively studied [1-3]. Recently our studies were concentrated on the reactions between carbon suboxide and some alkyne derivatives bearing either a hydroxy or an amino group, to synthesize heterocyclic compounds of potential biological interest [4].

In this present paper we wish to report on the synthesis of some new bicyclo and tricyclo derivatives obtained by reacting carbon suboxide and alkynes in three different molar ratios.

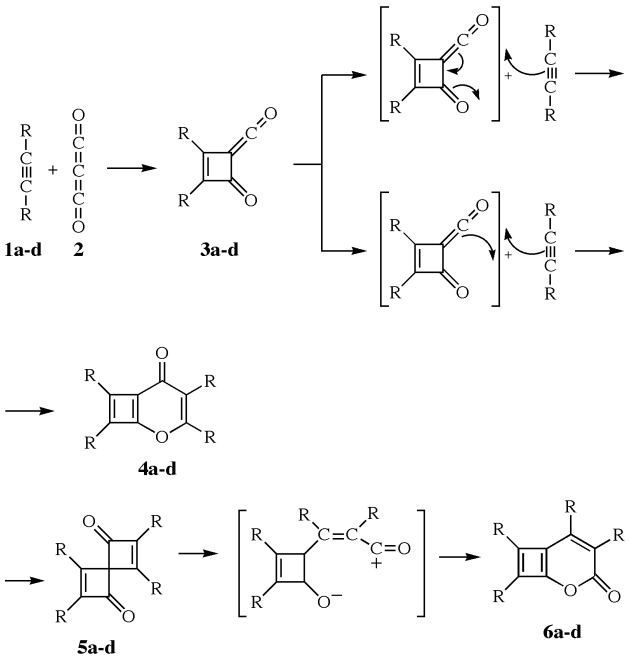
3,4,7,8-Tetraalkyl-2-oxa-bicyclo[4.2.0]octa-1(6),3,7-trien-5-ones (**4a-d**) and 4,5,7,8-tetraalkyl-2-oxa-bicyclo-[4.2.0]octa-1(6),4,7-trien-3-ones (**6a-d**) were obtained by reacting 0.032 mole of alkyne derivatives (**1a-d**) with 0.016 mole of carbon suboxide (**2**) in anhydrous chloroform solution. By using this ratio (2:1), yields are about 50%.

The proposed reaction mechanism starts from the attack of **1a-d** by **2** leading to the 4-oxomethylidene-2-cyclobuten-1-one derivatives (**3a-d**) followed by the attack of another **1a-d** molecule to achieve the compounds (**4a-d**) and (**6a-d**). Although intermediates **3a-d** were not isolated in this reaction, they have been previously reported by an Austrian researching group [5].

Analogously, though in a previous paper we described the structure and stability of similar spiroalkandiones [6], any attempt to isolate **5a-d** failed, since they rearranged to form **6a-d** (Scheme 1).

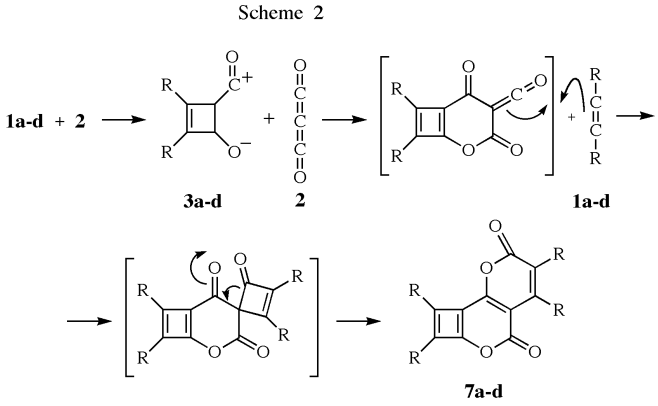
By reacting compounds **1a-d** with **2** in a 1:2 molar ratio, we obtained a gummy product, that was probably a polymer or a macrocycle, along with a small quantity of **4a-d** [7]. However, by reacting **1a-d** with **2** in a 2:2.5 molar ratio, we obtained the new 3,4,7,8-tetraalkyl-2*H*,5*H*-cyclobuta[*b*]pyrano[2,3-*d*]pyran-2,5-diones (**7a-d**), and a

Scheme 1



R: **a** = CH_3 **b** = C_2H_5, **c** = C_3H_7, **d** = C_6H_5

Scheme 2



R: **a** = CH_3 **b** = C_2H_5, **c** = C_3H_7, **d** = C_6H_5

Table 1

Spectral Data for Compounds (**4a-d**)

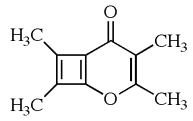
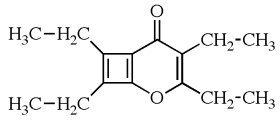
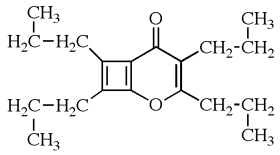
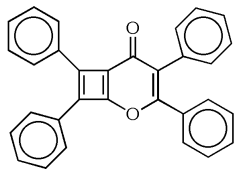
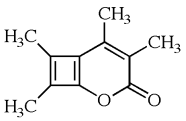
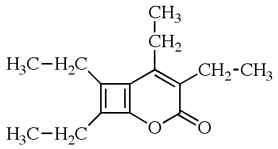
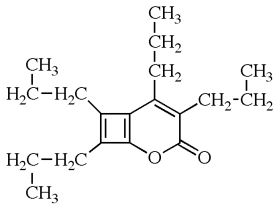
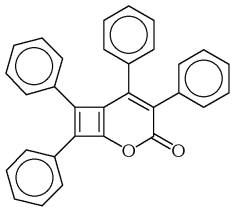
4a		1.85: s, 3H, CH_3 (4) 1.90: s, 3H, CH_3 (8) 1.98: s, 3H, CH_3 (7) 2.28: s, 3H, CH_3 (3)	193 = C5 161 = C3 160 = C1 133 = C7 131 = C8 108 = C4 105 = C6
4 b		1.02: t, 9H, $3CH_3$ (7,8,4), J= 9 Hz 1.07: t, 3H, CH_3 (3), J= 9.0 Hz 2.25: q, 2H, *CH_2*-CH_3 (4), J= 9 Hz 2.38: q, 2H, *CH_2*-CH_3 (3), J= 9 Hz 2.46: q, 4H, 2*CH_2*-CH_3 (8,7), J= 9 Hz	189 = C5 167 = C3 160 = C1 137 = C7 136 = C8 113 = C4 103 = C6
4 c		0.78: t, 3H, CH_3 (3), J= 9 Hz 0.90: t, 6H, $2CH_3$ (7,8), J= 9 Hz 0.95: t, 3H, CH_3 (4), J= 9 Hz 1.48: m, 2H, *CH_2*-CH_3 (3) 1.61: m, 6H, 3*CH_2*-CH_3 (7,8,4) 2.14: t, 2H, *CH_2*-CH_2 (4), J= 6.0 Hz 2.20: t, 2H, *CH_2*-CH_2 (3), J= 6.0 Hz 2.27: t,2H, *CH_2*-CH_2, (7), J= 6.0 Hz 2.37: t, 2H, *CH_2*-CH_2, (8), J= 6.0 Hz	191 = C5 172 = C3 163 = C1 138 = C7 136 = C8 118 = C4 107 = C6
4 d		7.70-7.29: m, 20H, Arom.	181 = C5 163 = C3 155 = C1 140 = C7 138 = C8 122 = C4 106 = C6

Table 2

Spectral data for compounds (**6a-d**).

6a		1.88: s, 3H, CH_3 (4) 2.01: s, 3H, CH_3 (7) 2.05: s, 3H, CH_3 (8) 2.11 : s, 3H, CH_3 (5)	161 = C3 147 = C5 146 = C1 136 = C7 131 = C8 128 = C6 120 = C4
6b		1.01: t, 6H, 2 CH_3 (7,5), J= 9 Hz 1.14: t, 6H, 2 CH_3 (8,4), J= 9 Hz 2.30: q, 4H, 2 *CH_2*-CH_3 (7,5), J= 9 Hz 2.49: q, 2H, *CH_2*-CH_3 (8), J= 9 Hz 2.60: q, 2H, *CH_2*-CH_3 (4), J= 9 Hz	158 = C3 147 = C5 145 = C1 141 = C7 131 = C8 128 = C6 95 = C4
6c		0.91: t, 9H, 3*CH_3*-CH_2 (7,8,5), J=9Hz 0.98: t, 3H, *CH_3*-CH_2 (4), J= 9 Hz 1.50: m, 4H, 2*CH_2*-CH_3 (5,4) 1.60: m, 4H, 2*CH_2*-CH_3) (7,8 2.17: t, 4H, 2 *CH_2*-CH_2 (7,5), J= 6 Hz 2.30: t, 2H, *CH_2*-CH_2 (4), J= 6 Hz 2.40: t,2H, *CH_2*-CH_2 (8), J= 6 Hz	159 = C3 151 = C5 148 = C1 142 = C7 133 = C8 132 = C6 109 = C4
6d		7.73-7.21: m, 20H, Arom.	160 = C3 152 = C5 149 = C1 142 = C7 138 = C8 133 = C6 123 = C4

small quantity of **4a-d** (Scheme 2). By using this ratio the reaction proceeds with satisfactory yields of the tricycle pyranone. The analytical and spectroscopic data of **4a-d**, **6a-d** and **7a-d** are reported in Tables 1-4.

The structures of all synthesized compounds were identified by both analytical and spectroscopic data. In particular, the structural differences between **4a-d** and **6a-d** derivatives were confirmed by FT IR spectra (γ-pyrone and α-pyrone carbonyl band respectively for **4a-d** and **6a-d** derivatives), and ^{13}C NMR spectra (significant carbonyl peak at *ca*. 180- 190 (ppm) for **4a-e** and 158-160 (ppm) for **6a-e**).

The most significant fragment ions in the mass spectra along with the elemental analysis of all the synthesized compounds confirmed the hypothesized structures.

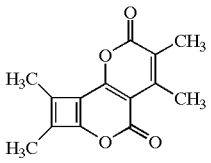
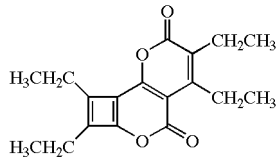
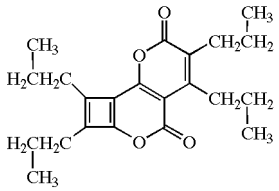
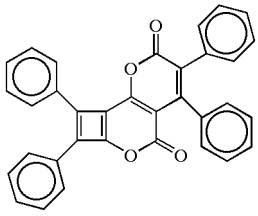
EXPERIMENTAL

Melting points were determined on a Köfler apparatus and are uncorrected. The FT IR spectra were recorded on a Perkin Elmer System 2000 spectrophotometer using KBr mulls. ^{13}C and ^{1}H NMR spectra were recorded on a Varian Unity 300 using TMS as an internal standard. MS spectra were recorded on a QMD 1000 instrument (Fisons instrument) in electron ionisation (e.i.) conditions (70 eV, source temperature 200 °C). Samples were introduced directly into the source. The analyses were carried out on a Carlo Erba Model 1106 Elemental analyser. Commercially available reagent-grade reagents and solvents were used. All compounds were purchased from Aldrich Chemical Co. and the solvents were dried rigorously before use according to standard methods.

Carbon suboxide was prepared from pyrolysis of di-*O*-acetyltartaric anhydride [8]. Silica gel 60, 230-400 mesh (Carlo Erba) was used for column chromatography.

Table 3

Spectral data for compounds (**7a-d**)

7a		2.04: s, 6H, $2CH_3$ (7,3) 2.14: s, 3H, CH_3 (8) 2.34: s, 3H, CH_3 (4)	162 = C2 160 = C5 152 = C8b 150 = C6a 145 = C4 132 = C7 130 = C8 124 = C3 123 = C8a 104 = C4a
7b		1.00: t, 3H, CH3 (8), J= 9 Hz 1.13: t, 9H, 3 CH_3 (7,4,3) 2.33: q, 4H, 2 CH_2 (8,4), J= 9 Hz 2.47: q, 2H, CH_2 (7), J= 9 Hz 2.58: q, 2H, CH_2 (3), J= 9 Hz	159.7=C2 158 = C5 150 = C8b 148 = C6a 144 = C4 136 = C7 135 = C8 119 = C3 110 = C8a 95 = C4a
7c		0.86: 9H, 3 CH_3 (7,8,4) 0.97: t, 3H, CH_3 (3), J= 6 Hz 1.70-1.49: 8 H, 4 CH_2CH_3 (7,8,4,3) 2.19: t, 4H, 2 CH_2CH_2 (8,4), J= 3 Hz 2.40: t, 4H, 2 CH_2CH_2 (7,3), J= 3 Hz	161 = C2 159 = C5 152 = C8b 150 = C6a 148 = C4 137 = C7 135 = C8 125 = C3 116 = C8a 103 = C4a
7d		7.86-7.20: m, 20H, Arom.	159 = C2 157 = C5 155 = C8b 154 = C6a 150 = C4 140 = C7 139 = C8 130-127= C(Arom) 126 = C3 125 = C8a 107 = C4a

General Procedure for the Preparation of 3,4,7,8-Tetraalkyl-2-oxa-bicyclo[4.2.0]octa-1(6),3,7-trien-5-ones (**4a-d**), and 4,5,7,8-Tetraalkyl-2-oxa-bicyclo[4.2.0]octa-1(6),4,7-trien-3-ones (**6a-d**).

Carbon suboxide (**2**) (1,10 g, 16 mmole) was added at -70 °C to a stirred solution of **1a-d** (32 mmole) in anhydrous chloroform (300 mL), stabilised with amylene. At completion the mixture was kept at -5 °C for 24 h, then at rt for 48 h while stirring continuously. At the end of the reaction, the solvent was evaporated under reduced pressure and the crude residue was purified by column chromatography (benzene:ethyl acetate 5:1 as eluents, the eluent ratio was varied by increasing the ethyl acetate until a benzene:ethyl acetate ratio of 1:1 was reached) to provide **4a-d** as first eluate and successively **6a-d**. The analytical and spectral data are listed in Tables 1, 2 and 4.

General Procedure for the Preparation of 3,4,7,8-Tetraalkyl-2*H*,5*H*-cyclobuta[*b*]pyrano[2,3-*d*]pyran-2,5-diones (**7a-d**).

Carbon suboxide (**2**) (2.75 g, 40 mmole) was added at -70 °C to a stirred solution of **1a-d** (32 mmole) in anhydrous chloroform

Table 4

Analytical and Spectral Data for Compounds (**4a-d, 6a-d** and **7a-d**)

	Yield (%)	Mp (°C)	FTIR (cm^{-1})	Elemental Analysis Calc. (%) (Found)	MS m/z	
4a	45	161-163	1750-1675-865-845-800	C:74.98; H:6.86 (74.95); (6.90)	176(M^+), 148(M-CO), 122(M-C_4H_6), 94(148-C_4H_6)	$C_{11}H_{12}O_2$
4b	52	169-172	1750-1675-860-850-790	C:77.55; H:8.68 (77.59); (8.70)	232(M^+), 204(M-CO), 150(M-C_6H_{10}), 122(204-C_6H_{10})	$C_{15}H_{20}O_2$
4c	55	175-177	1750-1675-960-845-790	C:79.12; H:9.78 (79.16); (9.81)	288(M^+), 260(M-CO), 150(M-C_8H_{14}), 110(C_8H_{14})	$C_{19}H_{28}O_2$
4d	47	198-199	1765-1675-1640-950-780	C:87.71; H:4.75 (87.69); (4.79)	424(M^+), 396(M-CO), 218(396-$C_{14}H_{10}$), 178($C_{14}H_{10}$)	$C_{31}H_{20}O_2$
6a	30	178-180	1655-1630-1150-1035-870	C:74.98; H:6.86 (75.00); (6.90)	176(M^+), 146(M-2CH_3), 132(M-CO_2), 116(M-4CH)	$C_{11}H_{12}O_2$
6b	48	180-182	1774-1620-1150-1070-1030	C:77.55; H:8.68 (77.51); (8.72)	232(M^+), 188(M-CO_2), 174-106-82	$C_{15}H_{20}O_2$
6c	51	187-189	1774-1630-1100-1030-955	C:79.12; H:9.78 (79.10); (9.75)	288(M^+), 244(M-CO_2), 134(244-C_8H_{14}), 110(C_8H_{14})	$C_{19}H_{28}O_2$
6d	60	209-210	1774-1630-1100-980-950	C:87.71; H:4.75 (87.75); (4.71)	424(M^+), 380(M-CO_2), 246(M-$C_{14}H_{10}$), 202(380-$C_{14}H_{10}$)	$C_{31}H_{20}O_2$
7a	53	205-207	1774-1645-1010-990-870	C:68.85; H:4.95 (68.89); (4.98)	244(M^+), 200(M-CO_2), 190(M-C_4H_6), 146(200-C_4H_6)	$C_{14}H_{12}O_4$
7b	58	210-112	1774-1640-1000-990-860	C:71.98; H:6.71 (72.00); (6.76)	300(M^+), 256(M-CO_2), 218(M-C_6H_{10}), 174(256-C_6H_{10})	$C_{18}H_{20}O_4$
7c	60	209-211	1774-1640-1080-990-930	C:74.13;H:7.92 (74.10); (7.96)	356(M^+), 312(M-CO_2), 246(M-C_8H_{14}), 202(312-C_8H_{14})	$C_{22}H_{28}O_4$
7d	67	217-219	1774-1640-1000-990-850	C:82.91;H:4.09 (82.84); (4.08)	492(M^+), 448(M-CO_2), 314(M-$C_{14}H_{10}$), 270(448-$C_{14}H_{10}$)	$C_{34}H_{20}O_4$

(600 mL), stabilised with amylene. At completion the mixture was kept at -5 °C for 24 h, then at rt for 72 h while stirring continuously. At the end of the reaction, the solvent was removed under reduced pressure and the crude residue was purified by column chromatography (benzene:acetone 5:1 as eluents, the eluent ratio was varied by increasing the acetone until a benzene:acetone ratio of 1:1 was reached) to provide **4a-d** as first eluate and successively **7a-d**. The analytical and spectral data are listed in Table 3 and 4.

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