SUBSTITUTED DIENIC 1,3-DIOXOLAN-2-ONES AND BIS(1,3-DIOXOLAN-2-ONES)

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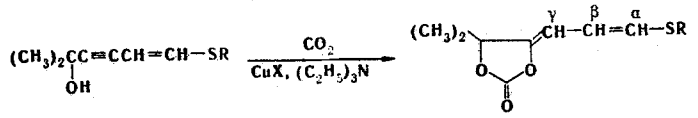
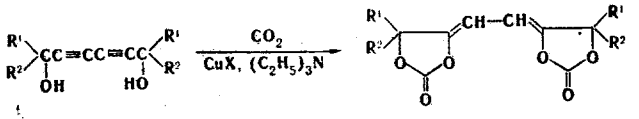
Alkylthio-substituted dienic 1,3-dioxolan-2-ones and bis(4,4-diorganyl-5-methylidene-1,3-dioxolan-2-ones) were obtained in high yields by the reaction of 2-methyl-6-alkylthio-5-hexen-3-yn-2-ols and tertiary diacetylenic glycols with carbon dioxide under pressure in the presence of catalytic amounts of triethylamine and monovalent copper salts.

The available information regarding the use of acetylenic alcohols for the synthesis of cyclocarbonates is limited [1]; no data pertaining to enyne carbinols (especially sulfur-containing compounds) and diacetylenic glycols are available.

For the first time we have accomplished the reaction of tertiary alkylthioenyne alcohols (Ia-d) [2] and ditertiary diacetylenic glycols (IIa-d) [3] with carbon dioxide under pressure in the presence of catalytic amounts of monovalent copper salts and triethylamine.



I a-d III a-d



II a-d IV a-d

I a III a R = C_2H_5; b R = *n*-Pr; c R = *n*-Bu; d R = *i*-Bu; II a IV a $R^1 = R^2 = CH_3$; b $R^1 = CH_3$, $R^2 = C_2H_5$; c $R^1 = R^2$ = *n*-Pr; d $R^1 - R^2 = (CH_2)_4$; X = Cl, OAc

Because of the high reactivity of alkylthioenyne alcohols and the presence in them of a sulfur atom, which is capable of complexing with copper salts, and of an enyne grouping, which is inclined to undergo polymerization via both radical and ionic mechanisms, the possibility of the efficient realization of this reaction was not obvious.

The investigated reaction leads to the formation of 4,4-dimethyl-5-(3-alkylthio-2-propenylidene)-1,3-dioxolan-2-ones (IIIa-d) in 70-95% yields.

These compounds are yellow crystalline (except for IIIb) substances with relatively low melting points that are stable during storage (Table 1). Absorption bands corresponding to Me_2C (1370-1375 and 1390 cm^{-1}), C=C-S (1580-1590 cm^{-1}), HC=(3050-3055 cm^{-1}), and C=C-O-C=O (1690-1695 cm^{-1}) groupings and the $\begin{matrix} O \\ O \end{matrix}\!\!>\!C{=}O$ grouping in a five-membered ring [4] (1822-1830 and 1842-1853 cm^{-1}) are observed in their IR spectra. The PMR spectra (Table 2) are also in agreement with 1,3-dioxolan-2-one structure III.

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TABLE 1. Characteristics of the Compounds Obtained

Compound	mp, °C	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	S		C	H	S	
IIIa	73 (hexane)	55,9	6,5	14,9	$C_{10}H_{14}O_3S$	56,1	6,6	14,9	88[a] 85[b]
IIIb	—	57,8	7,1	14,4	$C_{11}H_{16}O_3S$	57,9	7,1	14,0	90[a] 70[b]
IIIc	42 (hexane)	59,8	7,4	13,2	$C_{12}H_{18}O_3S$	59,5	7,5	13,2	77[a] 89[b]
IIId	64 (hexane)	59,5	7,5	13,2	$C_{12}H_{18}O_3S$	59,5	7,5	13,2	90[a] 95[b]
IVa	215—217	56,4	5,7	—	$C_{12}H_{14}O_6$	56,7	5,6	—	92[a]
IVb	183—185	59,8	6,5	—	$C_{14}H_{18}O_6$	59,6	6,4	—	96[a]
IVc	180—183	65,9	8,3	—	$C_{20}H_{30}O_6$	65,6	8,3	—	98[a]
IVd	182—185	62,6	5,7	—	$C_{16}H_{18}O_6$	62,8	5,9	—	97[a]

[a]With CuCl as the catalyst. [b]With CuOAc as the catalyst.

TABLE 2. PMR Spectra of 1,3-Dioxolan-2-ones III and Bis(1,3-dioxolan-2-ones)

Compound	Chemical shifts, δ, ppm							
	Me	$(Me)_2C$	SCH_2	H_α[a]	H_β[a]	H_γ[a]	CH_2	=CH
IIIa	1,30 t	1,61 s	2,70 q	5,96 d	6,30 q	5,40 d	—	—
IIIb	0,98 t	1,60 s	2,65 m	5,97 d	6,25 q	5,43 d	—	—
IIIc	0,85 t	1,60 s	2,67 m	5,97 d	6,25 q	5,40 d	—	—
IIId	0,97 d (*i*-BuS)	1,60 s	2,56 d	5,90 d	6,27 q	5,38 d	—	—
IVa	—	1,68 s	—	—	—	—	—	5,6 s
IVb	1,64 s 0,9 t (Et)	—	—	—	—	—	1,85 q	5,64 s
IVd	—	—	—	—	—	—	2,05 m	5,68 s

[a]In the case of IIIa-d, $J^{cis}_{H_\alpha H_\beta} \approx 10$ Hz and $^3J_{H_\beta H_\gamma} \approx 11$ Hz.

Ditertiary diacetylenic glycols IIa-d react with carbon dioxide at both hydroxy groups to give bis(4,4-diorganyl-5-methylidene-1,3-dioxolan-2-ones) (IVa-d) that contain a diene grouping between two 1,3-dioxolan-2-one rings. The stable, white, crystalline, high-melting products (IV) were obtained in > 90% yields based on the converted diacetylenic glycols. At the same time, the conversion of the starting ditertiary diols II is very low (2-40%). Extensive variation of the condensation conditions (the nature of the copper salt — CuCl, $CuSo_4$, and CuOAc), the amount of catalyst, the carbon dioxide pressure, and the temperature or reaction time and the use of organic solvents (acetone, methanol) do not lead to an increase in this parameter. The products are formed in only negligible yields in the presence of copper sulfate and acetate.

It should also be emphasized that the reaction of ditertiary diacetylenic glycols with carbon dioxide always leads to the production of bis(1,3-dioxolan-2-ones) IV rather than to the corresponding monoadducts.

The IR spectra of bis(1,3-dioxolan-2-ones) IV contain absorption bands corresponding to gem-dimethyl (1378 and 1390 cm^{-1} for IVa), methyl (1390 cm^{-1} for IVb or 1385 cm^{-1} for IVc), and cycloalkyl (1315 cm^{-1} for IVd) groups. The absorption bands common to the spectra of all IV are related to C=C–O–C=O groupings (1670-1680 cm^{-1}), the $\begin{matrix}O\\O\end{matrix}\!\!>\!C{=}O$ grouping in a five-membered ring (two bands at 1805-1845 cm^{-1} for IVa and IVc, and a single band at 1813 and 1815 cm^{-1} for IV b and IVd, respectively), and to the HC= group (3078-3080 cm^{-1}).

The data from the PMR spectra (Table 2) and the results of elementary analysis (Table 1) also constitute evidence in favor of the proposed bis(1,3-dioxolan-2-one) structure IV.

Dienic 1,3-dioxolan-2-ones III and IV may find application as monomers for polymerization and intermediates for fine organic synthesis and in the manufacture of dyes and medicinal preparations.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in CCl_4 were recorded with a Tesla BS-487C spectrometer (80 MHz) with tetramethylsilane as the internal standard; the accuracy in the determination of the chemical shifts was ± 0.01 ppm. The IR spectra of solutions of IIIa, c, d in CCl_4, a thin layer of IIIb, and KBr pellets of IVa-d were recorded with a UR-20 spectrometer with NaCl and LiF prisms at 600-3500 cm^{-1}.

4,4-Dimethyl-5-(3-ethylthio-2-propenylidene)-1,3-dioxolan-2-one (IIIa, Tables 1 and 2). A) A rotary autoclave was charged with 0.09 g (0.9 mmole) of cuprous chloride, 0.18 g (1.8 mmole) of triethylamine, 4.5 g (0.026 mole) of 2-methyl-6-ethylthio-5-hexen-3-yn-2-ol (Ia), and 80 g (1.82 mole) of dry carbon dioxide, and the mixture was heated at 70°C (and 70 atm gauge) for 7 h. It was then cooled to 20°C, and the yellow crystalline mass was dissolved in a small amount of ether. The solid material was removed by filtration, and the solvent was removed from the filtrate to give 4.2 g (88%) of IIIa.

B) Compound IIIa [5.32 g (85%)] was obtained from 0.1 g (0.8 mmole) of cuprous acetate, 0.2 g (1.6 mmole) of triethylamine, 5 g (0.029 mole) of carbinol Ia, and 80 g (1.8 mole) of dry carbon dioxide after heating at 70-75°C (and 70 atm gauge) for 7.5 h.

4,4-Dimethyl-5-(3-propylthio-2-propenylidene)-1,3-dioxolan-2-one (IIIb, Tables 1 and 2). A mixture of 0.1 g (1 mmole) of cuprous chloride, 0.2 g (2 mmole) of triethylamine, 5.6 g (0.03 mole) of 2-methyl-6-propylthio-5-hexen-3-yn-2-ol (Ib), and 51 g (1.15 mole) of dry carbon dioxide was heated at 80°C (and 70 atm gauge) for 12 h, after which the liquid product was dissolved in ether, and the inorganic residue was removed by filtration. The solvent was removed from the filtrate by vacuum distillation to give 6.27 g (90%) of IIIb with bp 155-159°C (3 mm) and n_D^{20} 1.5392.

Compounds IIIb (by method B), IIIc (80°C, 12 h, 80 atm gauge; 70°C, 8 h, 73 atm gauge), and IIId (70-75°C, 12 h, 85 atm gauge; 70°C, 16 h, 85 atm gauge) were similarly obtained (Tables 1 and 2).

Bis(4,4-dimethyl-5-methylidene-1,3-dioxolan-2-one) (IVa, Tables 1 and 2). A mixture of 0.1 g (1 mmole) of cuprous chloride, 0.16 g (1.6 mmole) of triethylamine, 2 g (0.012 mole) of 2,7-dimethyl-3,5-octadiyne-2,7-diol (IIa), and 85 g (1.93 mole) of dry carbon dioxide was stirred in an autoclave at 20-25°C (and 60 atm gauge) for 1 h and at 75-80°C (and 90-100 atm gauge) for 15 h, after which it was cooled to room temperature and dissolved in 70 ml of acetone. The precipitate was removed by filtration, the solvent was removed from the filtrate, and the residue was treated with methanol (the unconverted glycol dissolved in the latter) to give 0.7 g (92% based on the converted glycol) of crystalline IVa.

Compounds IVb-d were similarly obtained (Tables 1 and 2).

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