2. 3,3-Dichloroacetylacetone has less tendency to form adducts by homolytic addition than ethyl dichloroacetoacetate.

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OXIDATION OF ACETYLENYL-1,4-DIALYKOXYARENES BY $Ce(NH_4)_2(NO_3)_6$

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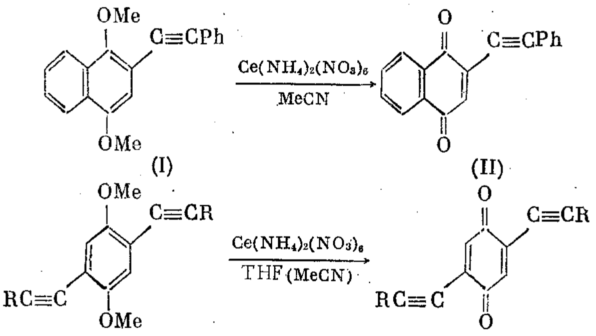
1,4-Dialkoxyarenes are oxidized by $Ce(NH_4)_2(NO_3)_6$ to quinones [1]. We have used this reaction to prepare compounds containing acetylenic substituents in the quinonoid ring.*



(I) (II) (III) (IVa—c)

R = Ph(a), p-$MeOC_6H_4$ (b), $HOCMe_2$ (c), p-$O_2NC_6H_4$ (d), PhCO (e), β-C_5H_4N (f), $O(CH_2CH_2)_2NCH_2$ (g), H (h)

The use of this method affords acetylenic derivatives of mono- and polynuclear quinones. 2-Phenylethynyl-1,4-naphthoquinone (II) and 2,5-di(phenylethynyl)-1,4-benzoquinone (IVa) were obtained from (I) and (IIIa) respectively in yields of 87 and 52%. The oxidation takes place satisfactorily if the acetylenic substituents contain electron-donating or weakly electron-accepting groups. Thus, 2,5-di(p-methoxyphenylethynyl)- (IIIb) and 2,5-bis(3'-hydroxy-3'-methyl-1'-butynyl)-1,4-dimethoxybenzene (IIIc) are readily converted into the quinones (IVb and c) in yields of 65 and 40%. Strongly electron-accepting groups such as p-$O_2NC_6H_4$ in (IIId) and PhCO in (IIIe) prevent reaction. 2,5-Di(β-pyridylethynyl)-1,4-dimethoxybenzene (IIIf) apparently forms a complex salt with $Ce(NH_4)_2(NO_3)_6$, which is insoluble in the reaction medium, and is not oxidized.

The presence in the side chain of functional groups which are readily oxidized by cerium(IV) can change the course of the reaction. 2,5-Bis(3'-N-morpholino-1'-propynyl)-1,4-dimethoxybenzene (IIIg), on reaction with $Ce(NH_4)_2(NO_3)_6$, does not give the expected quinone, but the unsaturated dialdehyde (V):

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*For the previous communication, see [2].

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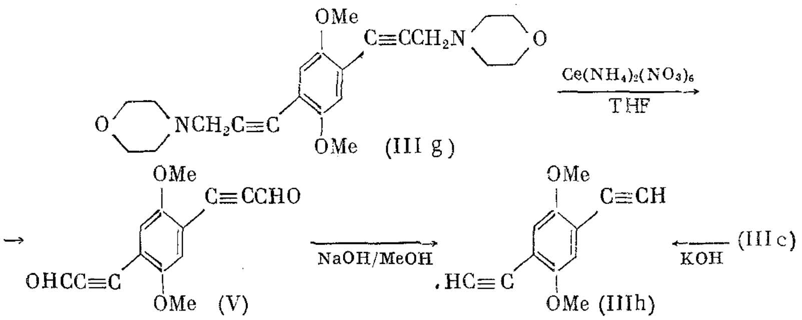
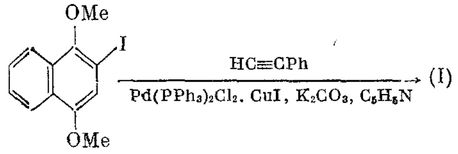
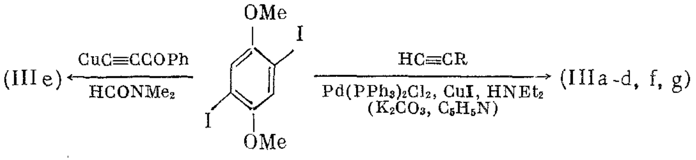


The structure of (V) was confirmed analytically and spectrally, and by decarbonylation to 2,5-diethynyl-1,4-dimethoxybenzene (IIIh), which was synthesized directly by alkaline fission of the diacetylenic glycol (IIIc).

In addition to the reason given above, the lack of success in obtaining certain acetylenylquinones may be due to their high chemical lability. It was probably for this reason that our attempt to synthesize 2,5-diethynyl-1,4-benzoquinone from (IIIh) was unsuccessful.

The acetylenyl-1,4-dimethoxyarenes (I) and (IIIa-d, f, and g) were synthesized by condensing 2-iodo-1,4-dimethoxynaphthalene (VI) and 2,5-diiodo-1,4-dimethoxybenzene (VII) with the appropriate terminal acetylenes under the conditions described in [3, 4], and (IIIe) was obtained by condensing (VII) with CuC≡CCOPh [5].


(VI)


(VII)

EXPERIMENTAL*

2-Iodo-1,4-dimethoxynaphthalene (VI). A 2.4-g sample of 2-amino-1,4-dimethoxynaphthalene hydrochloride [6] in 25 ml of dilute HCl (1:3) was diazotized at 0-5° with 0.8 g of $NaNO_2$ in 2 ml of water. Over a period of 2 h 8 g of KI in 20 ml of water was added, the temperature being raised slowly to 20°, and the product was extracted with ether. The extract was washed with water, aqueous $NaHCO_3$ and aqueous $Na_2S_2O_3$, and again with water, dried over K_2CO_3, and filtered through a column filled with layers of basic and neutral Al_2O_3 (grade II) (150×50 mm). Compound (VI) was crystallized from EtOH, yield 1 g (31.7%), mp 82.5-83°. Found: C 45.92; H 3.57; I 40.44%. $C_{12}H_{11}IO_2$. Calculated: C 45.88; H 3.53; I 40.40%. PMR spectrum (CCl_4, δ, ppm): 3.21, 3.87 (1- and 4-OCH_3), 6.90 (3-H), 7.2-8.2 m (5-, 6-, 7-, and 8-H).

2,5-Diiodo-1,4-dimethoxybenzene (VII). The dimethyl ether of hydroquinone (3.4 g), 5 g of I_2, and 2.6 g of HIO_3 in a mixture of 40 ml of AcOH, 7 ml of 30% H_2SO_4, and 8 ml of CCl_4 was heated for 1.5-2 h at 70-75°, cooled with ice water, and the crystals which separated were filtered off and recrystallized from 430 ml of EtOH. Yield 8.1 g (84.4%) (VII), mp 169.5-170.5°, cf. [7]. PMR spectrum ($CDCl_3$, δ, ppm): 3.80 (OCH_3), 7.23 (3- and 6-H).

ACETYLENE CONDENSATION OF IODIDES (VI) AND (VII)

2-Phenylethynyl-1,4-dimethoxynaphthalene (I). A 1.4-g sample of (VI), 0.7 g of phenylacetylene, 1.2 g of finely ground K_2CO_3, 30 mg of $Pd(PPh_3)_2Cl_2$, and 50 ml of CuI in 25 ml of pyridine were heated at 45-50° in an atmosphere of nitrogen for 8.5 h, until (VI)

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*A student of Kemerov State University, N. N. Fokin, assisted in carrying out the experiments.

TABLE 1. Acetylene Condensation of (VI) and (VII)

Product	Reaction time, h	Yield, %	mp, °C	Molecular formula	Found/calculated, %		IR spectrum, $\nu C{\equiv}C$, cm^{-1} ($CHCl_3$)
					C	H	
(I)	8,5	63,9	79,5–80,5 (hexane)	$C_{20}H_{16}O_2$	83,33 83,31	5,67 5,59	2217 (CCl_4)
(III a)	11	92,3	176–176,5 (C_6H_6)	$C_{24}H_{18}O_2$	85,06 85,18	5,38 5,36	2215, sh 2230
(III b)	20	93,0	195,5–196 (C_6H_6)	$C_{26}H_{22}O_4$	78,26 78,37	5,56 5,57	2215, sh 2230
(III c)	51	91,5	159–159,5 ($ClCH_2CH_2Cl$)	$C_{18}H_{22}O_4$	71,23 71,50	7,46 7,33	2232 [3605, 3410 br (OH)]
(III d)	23	86,5	302–303 ($MeNO_2$)	$C_{24}H_{16}N_2O_6$ *	67,15 67,29	3,97 3,76	2215, sh 2230
(III e)	7	57,2	232–233 (dioxane)	$C_{26}H_{18}O_4$	78,98 79,17	4,58 4,60	2210 [1645 (C=O)]
(III f)	5	87,0	204–205 (with decomp., EtOH)	$C_{22}H_{16}N_2O_2$ *	77,71 77,63	4,78 4,74	2220, sh 2235
(III g)	30	83,8	179,5–180,5 (EtOH)	$C_{22}H_{28}N_2O_4$ *	68,41 68,73	7,47 7,34	2235

*Found/calculated, N, %: 6.58/6.54 (IIId); 8.10/8.23 (IIIf); 7.13/7.29 (IIIg).

had all reacted (TLC, grade II alumina; benzene–petroleum ether, 1:1). After dilution with ether, the reaction mixture was filtered, washed with water, dilute HCl, and again with water, dried over K_2CO_3, and (I) isolated by chromatography on alumina (grade II) in benzene followed by crystallization from hexane. Yield and constants are given in Table 1. Similarly, from (VII) and phenylacetylene there was obtained (IIIa) (cf. Table 1).

2,5-Di-(p-anisylethynyl)-1,4-dimethoxybenzene (IIIb). A 3.9-g sample of (VII), 3.2 g of p-methoxyphenylacetylene, 70 mg of $Pd(PPh_3)_2Cl_2$, and 35 mg of CuI in 70 ml of Et_2NH were stirred for 20 h at 45-50° in an inert atmosphere, then diluted with $CHCl_3$ and filtered through a layer of alumina (grade II). Compound (IIIb) was purified by crystallization from benzene.

Similarly were obtained (IIIc, d, f, and g) (cf. Table 1).

2,5-Di(benzoylethynyl)-1,4-dimethoxybenzene (IIIe). A 2-g sample of (VII) and 2.7 g of $CuC{\equiv}CCOPh$ in 60 ml of dimethylformamide were heated for 7 h at 145-150° in an inert atmosphere, poured into water, and the solid filtered off. Compound (IIIe) was isolated by chromatography on Al_2O_3 (grade II) in dichloroethane.

2,5-Diethynyl-1,4-dimethoxybenzene (IIIh). A 400-mg sample of (IIIc) and 100 mg of powdered KOH were heated under a layer of Alkaren high-vacuum oil in a sublimation apparatus in a vacuum at 110-130° (1.5 mm). The sublimate of (IIIh) was separated from contaminating (IIIc) by chromatography on alumina (grade II) in ether. The yield of (IIIh) was 220 mg (89%), mp 153-154°, cf. [8].

OXIDATION OF ACETYLENYL-1,4-DIMETHOXYARENES (I) AND (III)

2-Phenylethynyl-1,4-naphthoquinone (II). To 0.24 g of (I) in 5 ml of MeCN was added over 10 min 1.4 g of $Ce(NH_4)_2(NO_3)_6$ in 2.5 ml of water. After stirring for 15 min, the mixture was diluted with $CHCl_3$, washed with water until neutral, and the solvent removed *in vacuo*. The residue was triturated with a small amount of cold ether, and filtered off. The yield of (II) was 0.18 g (87.3%), mp 147-148° (from ether), identical with a sample obtained by oxidation of 2-phenylethynylnaphthalene with CrO_3 in AcOH [2]. IR spectrum (CCl_4, ν, cm^{-1}): 2210 ($C{\equiv}C$), 1660, 1680 (C=O). PMR spectrum ($CDCl_3$, δ, ppm): 7.16 (3-H), 7.2-8.2 m (5-, 6-, 7-, and 8-H).

Similarly were obtained: (IVa), yield 52.2% (in THF), mp ~238-240° (decomp., from CCl_4) (heated rapidly, at ~3 deg/sec, otherwise the decomposition point is below the melting point). Found: C 85.79; H 4.11%. $C_{22}H_{12}O_2$. Calculated: C 85.70; H 3.92%. IR spectrum ($CHCl_3$, ν, cm^{-1}): 2217, sh 2200 ($C{\equiv}C$), 1670 (C=O).

(IVb), yield 64.9% (in THF), mp (on rapid heating) ~228-229° (decomp., from $CHCl_3$). Found: C 78.19; H 4.43%. $C_{24}H_{16}O_4$. Calculated: C 78.25; H 4.38%. IR spectrum ($CHCl_3$, ν, cm^{-1}): 2208 (C≡C), 1665 (C=O).

(IVc), yield 40% (in MeCN), mp (on rapid heating) ~210-212° (decomp., from ether) [2]. IR spectrum ($CHCl_3$, ν, cm^{-1}): 2227 (C≡C), 1670 (C=O); 3605 (OH).

Attempts to oxidize (IIId-f) with an excess of $Ce(NH_4)_2(NO_3)_6$ in aqueous dioxane or THF resulted in 70-85% recovery of starting material.

2,5-Di(formylethynyl)-1,4-dimethoxybenzene (V). To 1.54 g of (IIIg) in 100 ml of THF was added 8.80 g of $Ce(NH_4)_2(NO_3)_6$ in 12 ml of water, stirred for 1 h, the solvent removed *in vacuo*, and the residue diluted with 150 ml of water. The (V) was filtered off, washed thoroughly with water, air-dried, and recrystallized from dichloroethane; yield 0.45 g (46.5%), mp (on rapid heating) ~234-236° (decomp.). Found: C 69.24; H 3.94%. $C_{14}H_{10}O_4$. Calculated: C 69.42; H 4.16%. IR spectrum ($CHCl_3$, ν, cm^{-1}): 2195, sh 2205 (C≡C), 1662 (C=O). PMR spectrum ($CDCl_3$, δ, ppm): 3.82 (OCH_3), 7.01 (3- and 6-H), 9.40 (CHO).

Decarbonylation of Aldehyde (V). To a suspension of 160 mg of (V) in 5 ml of MeOH was added at 50° a solution of 1.6 g of NaOH in 4 ml of water, stirred for 0.5 h at this temperature, and extracted with $CHCl_3$. Yield 123 mg (~100%) of (IIIa).

CONCLUSIONS

1. A series of quinones containing acetylenic substituents in the quinone ring have been synthesized by oxidizing acetylenic derivatives of 1,4-dimethoxybenzene and 1,4-dimethoxynaphthalene with $Ce(NH_4)_2(NO_3)_6$.

2. 2,5-Bis(3'-N-morpholino-1'-propynyl)-1,4-dimethoxybenzene on reaction with $Ce(NH_4)_2(NO_3)_6$ undergoes oxidative deamination to the dialdehyde, 2,4-di(formylethynyl)-1,4-dimethoxybenzene.

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