Oxidation of alkylphenylacetylenes and dialkylacetylenes on palladium catalysts in DMSO

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Alkylphenyl- and dialkylacetylenes are oxidized by the DMSO—$PdCl_2$ or DMSO—Pd/C system to give the corresponding 1,2-diketones. Oxidation of these compounds, unlike that of diarylacetylenes, is less selective and is accompanied by the partial cleavage of triple bonds and formation of ketones, 1,3-diketones, and aromatic compounds as secondary condensation products.

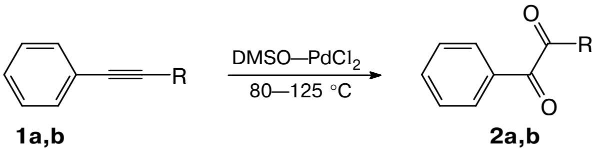
Key word: alkylphenylacetylenes, alkylacetylenes, diketones, dimethyl sulfoxide, palladium chloride.

Previously,[1—3] we have carried out successful oxidation of different diarylacetylenes and 1-phenylprop-1-yne (**1a**) under the action of DMSO in the presence of catalytic amounts of Pd/C or $PdCl_2$ to form 1,2-diketones. In these reactions, DMSO, which was converted into dimethyl sulfide, served as the true oxidant and oxidation proceded, apparently, through the conjugate addition of palladium and DMSO at the triple bonds.[4,5] In the present work, we studied oxidation of alkylaryl- and dialkylacetylenes **1a—d** by the DMSO—$PdCl_2$ or DMSO—Pd/C systems.

Results and Discussion

Oxidation of alkyne **1a** by DMSO—$PdCl_2$ was investigated in the temperature range of 80—125 °C (Scheme 1). In all cases, 1-phenylpropane-1,2-dione (**2a**) was obtained as the major product in 55—77% yields (Table 1), *i.e.*, oxidation of alkyne **1a** proceeded analogously to oxidation of tolan[3] but more rapidly. Apparently, insignificant resinification of the reaction mixture is associated with the fact that product **2a** contains the active ketomethylene fragment, which can be involved in different condensation reactions. As in the case of diarylalkynes, oxidation of alkyne **1** did not afford carboxylic acids (GLC and GLC/MS) and consequently, the triple bond was not cleaved. 1-Phenylpropan-2-one (**3**), which was the formal hydration product of alkyne **1a**, was isolated from the reaction mixture in a yield smaller than 1%; this was identified by GLC/MS. Oxidation in the presence of Pd/C instead of $PdCl_2$ proceeded much more slowly and diketone **2a** was obtained only in 10% yield within 25 h after the beginning of the reaction, the conversion of the initial alkyne **1a** also being low. The reaction was accelerated in the presence of $CuCl_2$, the initial alkyne disappeared after 5 h (GLC), and the yield of diketone **2a** was 67%. In the absence of Pd/C, copper salts in DMSO are inactive in these oxidation reactions.

Scheme 1



R = Me (**a**), Pr (**b**)

Oxidation of 1-phenylpent-1-yne (**1b**) differs from that of 1-phenylprop-1-yne (**1a**). In the former case, $PdCl_2$ is reduced to Pd^0 and the oxidation is retarded. Thus Pd precipitated as a black powder at 115 °C after 5 min. GLC analysis of the reaction mixture demonstrated that the content of diketone **2b** was 31 and 59% after 1 and 2 h, respectively. Further oxidation proceeded very slowly due apparently to the low concentration of $PdCl_2$, which is more active in the oxidation than Pd. Oxidation of alkyne **1b** at 90 °C was accompanied by the smallest resinification without reduction of $PdCl_2$ and the yield of diketone **2b** was 76% (see Table 1).

Reduction of $PdCl_2$ depends on its concentration and the reaction temperature. At the concentrations of $PdCl_2$ of 10 and 25%, reduction started at 100 and 85 °C, respectively. The reduction can be accounted for by the involvement of $PdCl_2$ in redox reactions of,

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Table 1. Oxidation of alkynes **1a,b** with the DMSO—$PdCl_2$ and DMSO—Pd/C—$CuCl_2 \cdot 2H_2O$ systems

Reagent	Substrate	T /°C	t /h	Product	Yield (%)
DMSO—$PdCl_2$	**1a**	80	19	**2a**	76
DMSO—$PdCl_2$	**1a**	90	12	**2a**	77
DMSO—$PdCl_2$	**1a**	100	3	**2a**	68[a]
DMSO—$PdCl_2$	**1a**	115	3	**2a**	67
DMSO—$PdCl_2$	**1a**	125	3	**2a**	59
DMSO—Pd/C	**1a**	105	25	**2a**	10[b]
DMSO—Pd/C— —$CuCl_2 \cdot 2H_2O$	**1a**	115	5	**2a**	67
DMSO—$PdCl_2$	**1b**	90	15	**2b**	76
DMSO—$PdCl_2$	**1b**	100	1.5	**2b**	55[a]
DMSO—$PdCl_2$	**1b**	115	1.5	**2b**	59[c]
DMSO—Pd/C— —$CuCl_2 \cdot 2H_2O$	**1b**	105	27	**4**	86

[a] Under an atmosphere of N_2.

[b] The presence of the initial alkyne **1a** (56%) was established by GLC.

[c] The formation of Pd as a black powder was observed and the initial alkyne **2b** was isolated in 12% yield (GLC).

apparently, the methylene groups of the propyl fragment rather than of the triple bond. A similar reduction process of $PdCl_2$ has been observed previously[3] in the oxidation of 2,7-bis(phenylethynyl)fluorene giving rise to 2,7-bis(phenyldioxoethyl)fluorenone instead of the expected 2,7-bis(phenyldioxoethyl)fluorene. We believe that the oxidation of the methylene group follows the appearance of the carbonyl groups, because the reduction of palladium was observed only after the formation of diketone **2b**. The reaction of diketone **2b** with the DMSO—$PdCl_2$ system at 105 °C also afforded Pd^0 as well as benzoic acid (**4**) (8.5% after 1.5 h).

Under the action of the DMSO—Pd/C—$CuCl_2 \cdot 2H_2O$ system on alkyne **1b**, only acid **4** (86%) was obtained instead of the expected diketone **2b**. In the absence of $CuCl_2 \cdot 2H_2O$, oxidation proceeded very slowly and diketone **2b** was obtained in low yield (10%) after 25 h, the degree of conversion of the initial alkyne being also low. Thus, the presence of $CuCl_2 \cdot 2H_2O$ favors apparently the oxidation of alkyne **1b** to tetraketone $PhCOCOCOCOCH_3$, which is unstable and is converted into benzoic acid, as in the case of oxidation of diphenylbutadiyne.[2] The reaction afforded butyric acid (**5**) along with benzoic acid. The former was identified by GLC/MS. This fact suggests also the cleavage of the C—C bond between the adjacent carbonyl groups in diketone **2b**.

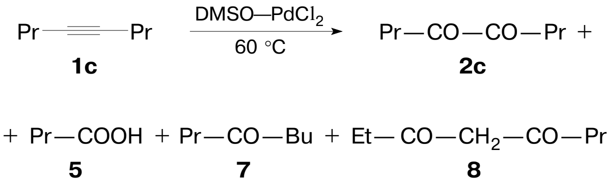
As in the case of phenylpropyne **1a**, an admixture of the product of formal hydration of the triple bond, *viz.*, 1-phenylpentan-2-one (**6**), was detected in the reaction mixture by GLC/MS.

Oxidation of alkynes **1a** and **1b** under an atmosphere of N_2 did not lead to an increase in the yields of diketones **2a** and **2b** and also did not preclude partial resinification of the reaction mixture. Below 80 °C, the reaction proceeded much more slowly and the target diketones **2a,b** were obtained in yields of no higher than 77%.

Oxidation of dialkylacetylenes, *viz.*, of oct-4-yne **1c** and tetradec-7-yne **1d**, differs from that of **1a**. The conversions of the former compounds into 1,2-diketones were not the major reaction pathways.

Oxidation of oct-4-yne **1c** with the DMSO—$PdCl_2$ system (Scheme 2) was carried out in the temperature range of 55—90 °C. In this case, the formation of metallic palladium and substantial resinification of the reaction mixture were also observed. Dilution of DMSO with benzene or methanol did not eliminate resinification of the reaction mixture. Oxidation of oct-4-yne at 60 °C afforded a mixture of four major products identified by GLC/MS as acid **5** (17%), octan-4-one (**7**) (9%), octane-4,5-dione (**2c**) (20%), and octane-3,5-dione (**8**) (52%).

Scheme 2



Oxidation of alkyne **1c** with $PdCl_2$ in a 3 : 1 DMSO—MeOH mixture at 60 °C or with $PdCl_2$—$CuCl_2 \cdot 2H_2O$ in a 3 : 1 C_6H_6—DMSO mixture at 80 °C are even more complicated processes. In the former case, acid **5** and octan-4-one **7** along with a mixture of at least six isomeric compounds with the molecular mass of 344 were detected in the reaction mixture by GLC/MS. The data from mass spectrometry for two of these compounds are in favor of structures **9** and **10** (Scheme 3, Table 2). The probable structural formula of the remaining four compounds (**11—14**) were suggested based on the mass spectra (Scheme 4, see Table 2). As would be expected for alkyl aryl ketones,[6,7] the mass spectra of compounds **9** and **11—14** have the most intense peaks of the molecular ions $[ArC{\equiv}O]^+$. Further fragmentation of these ions occurred as the loss of both the CO molecule (the necessary stage of fragmentation of the majority of mononuclear aromatic ketones)[6,7] and the C_2H_4 molecule. These results suggest that the reaction of oct-4-yne with $PdCl_2$ in the DMSO—MeOH mixture involved trimerization of two oct-4-yne molecules and one molecule of diketone **2c** or **8**. Trimerization of two molecules of octan-4-one **7** with one molecule of diketone **2c** or **8** (see Scheme 4) is also not ruled out.

Six major reaction products were detected by GLC/MS when the reaction was carried out in benzene instead of MeOH. Two of these products were 1,2-diketone **2c** and trimerization product **10**. The ^{13}C NMR

Scheme 3

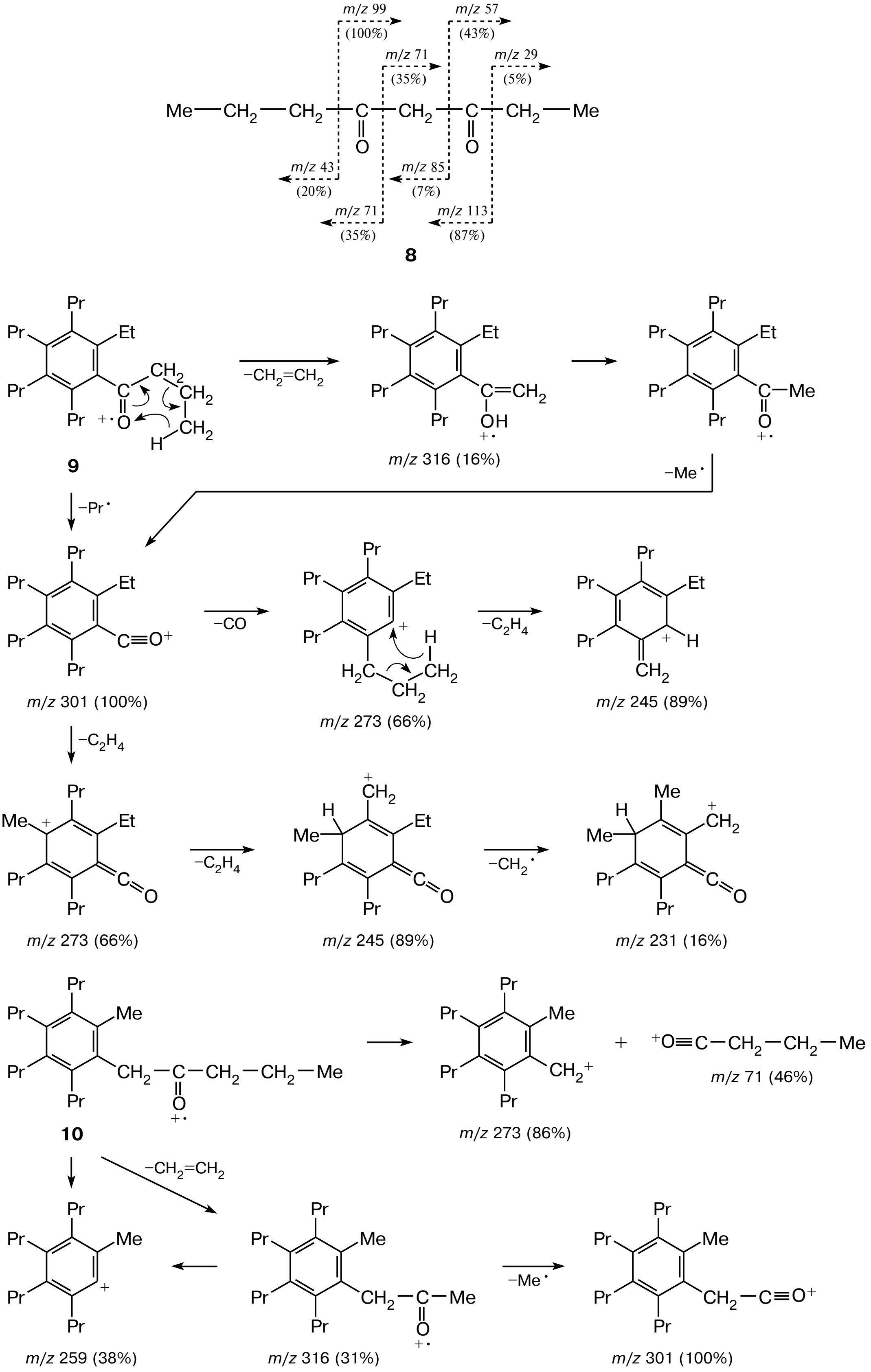

m/z 99 (100%)
m/z 57 (43%)
m/z 71 (35%)
m/z 29 (5%)
Me—CH2—CH2—C(=O)—CH2—C(=O)—CH2—Me
m/z 43 (20%)
m/z 85 (7%)
m/z 71 (35%)
m/z 113 (87%)
8
9
−CH2=CH2
m/z 316 (16%)
−Me•
−Pr•
m/z 301 (100%)
−CO
m/z 273 (66%)
−C2H4
m/z 245 (89%)
−C2H4
m/z 273 (66%)
−C2H4
m/z 245 (89%)
−CH2•
m/z 231 (16%)
10
+O≡C−CH2−CH2−Me
m/z 273 (86%)
m/z 71 (46%)
−CH2=CH2
m/z 259 (38%)
m/z 316 (31%)
−Me•
m/z 301 (100%)

Table 2. Characteristics of mass spectra of compounds **2a—c**, **3**, **6**, and **8—14**

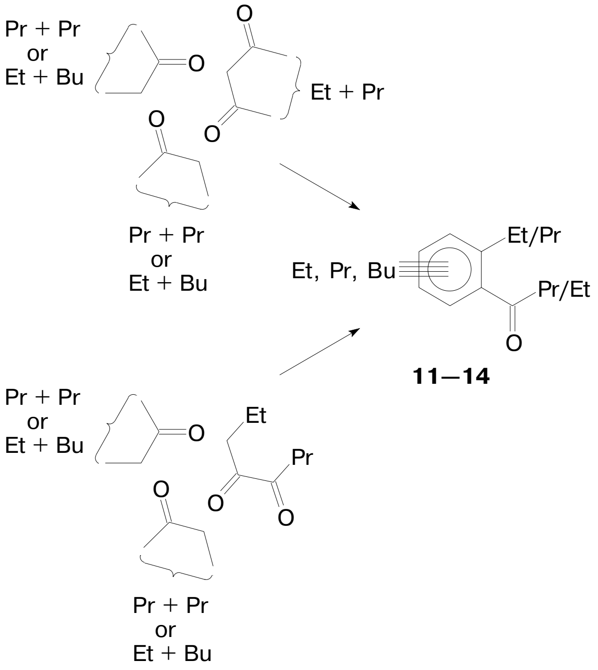
Compound	MS (EI, 70 eV), *m/z* (I_{rel} (%))
2a	148 $[M]^+$ (5), 105 $[PhCO]^+$ (100), 77 $[Ph]^+$ (48), 51 $[C_4H_3]^+$ (16)
2b	176 $[M]^+$ (4), 147 $[M - Et]^+$ (2), 105 $[PhCO]^+$ (100), 77 $[Ph]^+$ (52), 51 $[C_4H_3]^+$ (19), 43 $[Pr]^+$ (12)
2c	142 $[M]^+$ (8), 113 $[M - Et]^+$ (2), 71 $[C_4H_7O]^+$ (100), 55 $[C_3H_3O]^+$ (10), 43 $[C_2H_3O]^+$ (71), 27 $[C_2H_3]^+$ (14)
3	134 $[M]^+$ (57), 91 $[M - C_2H_3O]^+$ (100), 65 $[C_5H_5]^+$ (16), 43 $[C_2H_3O]^+$ (91)
6	162 $[M]^+$ (19), 91 $[M - C_4H_7O]^+$ (43), 71 $[C_4H_7O]^+$ (100), 65 $[C_5H_5]^+$ (14), 43 $[Pr]^+$ (40)
8	142$[M]^+$ (36), 114 $[M - C_2H_4]^+$ (15%), 113 $[M - Et]^+$ (87), 99 $[M - Pr]^+$ (100), 85 $[M - C_3H_5O]^+$ (7), 71 $[C_4H_7O]^+$ (35), 57 $[C_3H_5O]^+$ (43), 43 $[Pr]^+$ (20)
9	344 $[M]^+$ (44), 316 (16), 301 (100), 273 (66), 245 (89), 231 (16), 215 (21), 203 (6), 189 (11), 161 (5), 147 (5), 133 (4), 131 (7), 119 (7), 71 (31), 43 (13)
10	344 $[M]^+$ (36), 316 (31), 301 (100), 273 (86), 259 (38), 245 (24), 231 (36), 203 (11), 201 (12), 189 (10), 185 (10), 161 (7), 159 (10), 147 (10), 71 (46), 43 (6)
11	344 $[M]^+$ (24), 316 (5), 301 (14), 273 (100), 245 (11), 231 (11), 217 (11), 203 (6), 189 (7), 161 (4), 147 (4), 133 (4), 131 (5), 71 (29), 43 (10)
12	344 $[M]^+$ (25), 316 (5), 301 (23), 273 (100), 245 (13), 231 (20), 217 (5), 203 (6), 189 (5), 133 (4), 71 (7), 43 (4)
13	344 $[M]^+$ (24), 316 (6), 301 (20), 273 (100), 245 (11), 231 (21), 217 (7), 203 (6), 189 (4), 161 (4), 133 (4), 43 (3)
14	344 $[M]^+$ (44), 316 (5), 301 (26), 273 (100), 245 (14), 231 (11), 201 (12), 189 (7), 147 (4), 71 (10), 43 (4)

spectrum of the mixture following its chromatographic purification on silica gel had at least 6 signals in the region of δ 196.6—211.01, 29 signals in the region of aromatic and unsaturated C atoms (δ 115.07—160.73), and more than 45 signals in the region of aliphatic C atoms (δ 14.06—62.95).

Oxidation of tetradec-7-yne **1d** in DMSO containing $PdCl_2$—$CuCl_2 \cdot 2H_2O$ at 70 °C also gave rise to a complex mixture of reaction products. Hexanoic acid (6%), heptanoic acid (2%), tetradecan-7-one (41%), and tetradecane-7,8-dione (**2d**) (32%) were identified in the reaction mixture by GLC/MS. The absence of β-diketone and the high yield of α-diketone **2d** indicate that hydration and oxidation of alkyne **1d** were the major processes in this reaction.

Previously,[8] hydration of acetylenic ketones in a 10 : 1 acetonitrile—water mixture containing $PdCl_2(CN)_2$ with sonication was examined. In the case of dec-7-yn-2-one, a trimerization product of the initial alkyne along with the corresponding 1,6- and 1,7-diketones were obtained, but oct-1-yne and dec-5-yne remained intact.[8]

Scheme 4



11—14

Thus, hydration and oxidation of alkylphenylacetylenes and dialkylacetylenes with DMSO—$PdCl_2$ to 1,2-diketones are accompanied by the previously unknown reactions giving rise to 1,3-diketones and alkyl aryl ketones.

Experimental

The IR spectra were recorded on a Mattson 5000 spectrophotometer in thin films or in KBr pellets. The ^1H and ^{13}C NMR spectra were measured on a Bruker AC-300 spectrometer (300 MHz) with Me_4Si as the internal standard using $CDCl_3$ as the solvent. The GLC-mass spectra were obtained on a Hewlett Packard 5890/II gas chromatograph equipped with a quadrupole mass spectrometer (HP MSD 5971) as the detector (EI, 70 eV) and a 30-m×0.25-mm HP-5 quartz column with a copolymer of diphenyl- (5%) and dimethylsiloxane (95%) as the stationary phase (0.25 μm). Melting points were determined on an Electrothermal-9100 instrument. GLC was carried out on a Young Model 680A chromatograph equipped with a flame ionization detector and a 6FT10#OV-101 WHP 100/120 column with nitrogen as the carrier gas. Column chromatography was performed on Silica gel 60 G (Merck). TLC was carried out on Silica gel 60 F_{254} plates (Merck) using hexane or a 5 : 1 hexane—benzene mixture as the eluent. Alkynes **1a—c** were purchased from Aldrich. Dimethyl sulfoxide and $PdCl_2$ of the "chemically pure" grade were used without additional purification; Pd/C was a commercial catalyst containing 0.8% of palladium.

1-Phenylpropane-1,2-dione (2a). Palladium chloride (36 mg, 0.2 mmol) was added to a solution of 1-phenylprop-1-yne (**1a**) (232 mg, 2 mmol) in DMSO (5 mL). The reaction mixture was stirred at 90 °C for 12 h, diluted with water (30 mL), and extracted with ether (3×30 mL). The ethereal layer was washed with water (20 mL) and a saturated NaCl solution (20 mL) and then dried with Na_2SO_4. The solvent was distilled off *in vacuo* and the residue was chromatographed on silica gel (hexane—benzene, 5 : 1). 1-Phenylpropan-2-one (**3**) and diketone **2a** were obtained in yields of 3.0 mg (1%) and 228 mg (77%), respectively. Diketone **2a** was obtained as a yellow viscous liquid, n_D^{17} 1.5350; bis-4-nitrophenylhydrazone, m.p. 254—256 °C (*cf.* lit. data:[9] m.p. 254—255 °C). IR of **2a** (oil), ν/cm^{-1}: 1674, 1712 (C=O). ^{1}H NMR (CCl_4), δ: 2.45 (s, 3 H, CH_3); 7.20—7.50 (m, 3 H, H arom.); 7.95 (dd, 2 H, H arom., J = 2.0 and 8.0 Hz).

1-Phenylpentane-1,2-dione (2b). Palladium chloride (36 mg, 0.2 mmol) was added to a solution of 1-phenylpent-1-yne (**1b**) (288 mg, 2 mmol) in DMSO (5 mL) and the reaction mixture was stirred at 90 °C for 15 h. Subsequent workup was carried out as described above. Diketone **2b** was obtained as a yellow viscous liquid in a yield of 268 mg (76%). IR of **2b** (oil), ν/cm^{-1}: 1672, 1712 (C=O). ^{1}H NMR (CCl_4), δ: 1.07 (t, 3 H, CH_3, J = 7.0 Hz); 1.73 (m, 2 H, $C(4)H_2$); 2.83 (t, 2 H, $C(3)H_2$, J = 7.0 Hz); 7.46 (m, 3 H, H arom.); 8.00 (dd, 2 H, H arom., J = 2.0 and 8.0 Hz). Found (%): C, 75.04; H, 6.79. $C_{11}H_{12}O_2$. Calculated (%): C, 74.97; H, 6.87.

Oxidation of 1-phenylpent-1-yne (1b) with the DMSO—Pd/C—$CuCl_2 \cdot 2H_2O$ system. Pd/C (100 mg) and $CuCl_2 \cdot 2H_2O$ (34 mg, 0.2 mmol) were added to a solution of 1-phenylpent-1-yne (**1b**) (144 mg, 1 mmol) in DMSO (5 mL) and the reaction mixture was stirred at 105 °C for 27 h. After cooling, propan-2-ol (5 mL) was added and the catalysts was filtered off. The filtrate was diluted with a saturated solution of NaCl (20 mL) and extracted with ether (2×30 mL). The ethereal layer was washed with water (20 mL) and a saturated solution of NaCl (20 mL) and then dried with Na_2SO_4. The solvent was distilled off *in vacuo* and benzoic acid (**4**) was obtained in a yield of 105 mg (86%), m.p. 123—125 °C (*cf.* lit. data:[10] m.p. 122.5 °C).

Oxidation of oct-4-yne (1c) with the DMSO—$PdCl_2$ system. Palladium chloride (18 mg, 0.1 mmol) was added to a solution of oct-4-yne (**1c**) (110 mg, 1 mmol) in DMSO (5 mL). The reaction mixture was stirred at 60 °C for 32 h, diluted with water (30 mL), and extracted with ether (3×30 mL). The ethereal layer was washed with water (20 mL) and a saturated solution of NaCl (20 mL) and then dried with Na_2SO_4. The solvent was distilled off *in vacuo*. The residue was dissolved in hexane and passed through a layer of silica gel (h = 2 cm). The hexane was distilled off *in vacuo* and an oily pale-yellow liquid was obtained in a yield of 95 mg. The product was analyzed by GLC-mass spectrometry in the linear temperature programming mode from 60 to 240 °C (8 °C min^{-1}). The mixture contained butyric acid (**5**) (17%, T_R 15.94 min), octan-4-one (**7**) (9%, T_R 22.86 min), octane-3,5-dione (**8**) (52%, T_R 28.98 min), and octane-4,5-dione (**2c**) (20%, T_R 30.18 min).

Oxidation of oct-4-yne (1c) with the DMSO—$PdCl_2$—MeOH system. Palladium chloride (18 mg, 0.1 mmol) and $CuCl_2 \cdot 2H_2O$ (34 mg, 0.2 mmol) were added to a solution of oct-4-yne (110 mg, 1 mmol) (**1c**) in MeOH (5 mL) and DMSO (2.5 mL) and the reaction mixture was stirred at 60 °C for 10 h. Subsequent workup was carried out as described above. An oily product that crystallized was obtained in a yield of 106 mg. Analysis by GLC/MS performed in the linear temperature programming mode from 100 to 240 °C (10 °C min^{-1}) revealed the presence of octan-4-one (**7**) (6%, T_R 8.50 min) and a mixture of compounds **9—14** (the total yield was 92%, T_R 13.49, 14.20, 15.90, 23.34, 24.39, and 24.99 min, respectively).

Oxidation of oct-4-yne (1c) with the DMSO—$PdCl_2$—C_6H_6 system. Palladium chloride (28 mg, 0.157 mmol) and $CuCl_2 \cdot 2H_2O$ (53 mg, 0.2 mmol) were added to a solution of oct-4-yne (**1c**) (173 mg, 1.57 mmol) in benzene (6.0 mL) and DMSO (2.0 mL). The reaction mixture was stirred at 80 °C for 35 h, diluted with water (30 mL), and extracted with ether (3×30 mL). The ethereal layer was washed with water (20 mL) and a saturated solution of NaCl (20 mL) and then dried with Na_2SO_4. The solvent was distilled off *in vacuo* and a dark resin was obtained in a yield of 200 mg. This was chromatographed on silica gel (hexane) and an oily pale-yellow liquid was obtained in a yield of 97 mg. According to the GLC data, the mixture contained 14% of diketone **2c**. Analysis by GLC/MS in the linear temperature programming mode from 60 to 240 °C (8 °C min^{-1}) demonstrated that the reaction mixture contained butyric acid (**5**) (3%, T_R 15.87 min), octan-4-one (**7**) (5%, T_R 23.26 min), diketone **2c** (27%, T_R 29.95 min), and a mixture of compounds **9—14** (the total yield was 46%, T_R 62.87—70.08 min).

Oxidation of tetradec-7-yne (1d) with the DMSO—$PdCl_2$—$CuCl_2 \cdot 2H_2O$ system. Palladium chloride (18 mg, 0.1 mmol) and $CuCl_2 \cdot 2H_2O$ (34 mg, 0.2 mmol) were added to a solution of tetradec-7-yne (**1d**) (194 mg, 1 mmol) in DMSO (5 mL). The reaction mixture was stirred at 70 °C for 9 h and worked up in a manner analogous to that described for the oxidation of **1c**. An oily pale-yellow liquid was obtained in a yield of 187 mg. Analysis by GLC/MS in the linear temperature programming mode from 80 to 240 °C (10 °C min^{-1}) demonstrated that the reaction mixture contained hexanoic acid (6%, T_R 8.63 min), heptanoic acid (2%, T_R 13.04 min), tetradecan-7-one (41%, T_R 35.54 min), and tetradecane-7,8-dione (32%, T_R 38.19 min).

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