262. A New Reaction of 1,2-Dioxetanes

Formation of 1,2,4-Trioxanes from Aldehydes

by **Charles W. Jefford ***, **John Boukouvalas** and **Shigeo Kohmoto**

Department of Organic Chemistry, University of Geneva, CH-1211 Geneva 4

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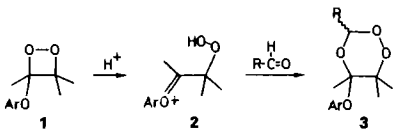
Summary

1,2-Dioxetanes bearing different 3-phenoxy substituents add to aldehydes to give 1,2,4-trioxanes in yields of 17–75% depending on the nature of the *para*-phenyl substituent. Illustrations of this new reaction are described.

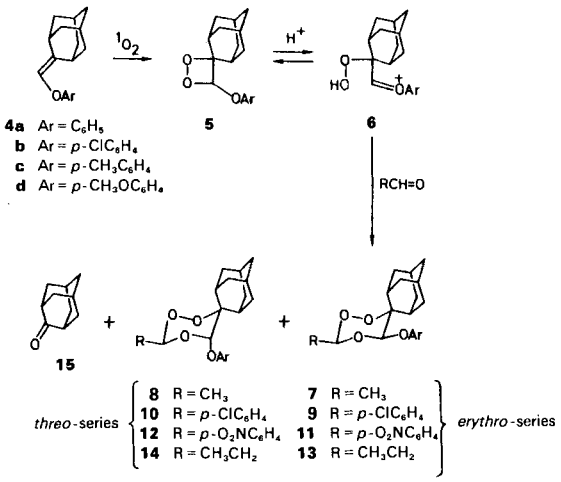
Introduction. – The number of reactions which 1,2-dioxetanes can undergo with organic molecules is strictly limited [1]. Usually initial scission of the O-O bond occurs, followed by attack of the reagent. We now report a new reaction of 1,2-dioxetanes **1** in which the key step is breaking of the C-O bond. This regioselectivity is conferred by a 3-phenoxy substituent. Dioxetanes so substituted **1** open easily on protonation to give the stable β-hydroperoxy phenoxonium cation **2** [2] *(Scheme 1)*. When **2** is generated in the presence of an aldehyde (RCHO), immediate reaction ensues to incorporate the carbonyl function, thereby forming the corresponding 1,2,4-trioxane **3**. The examples which follow demonstrate this novel mechanism, nonetheless the reaction may be of potential utility as it would offer a simple, mild means of preparing derivatives of a little known class [3] of heterocycles of which the most noteworthy member is 'Qinghaosu' [4].



Results. – The four 1,2-dioxetanes selected **5a–d** were prepared from the phenoxymethylideneadamantanes **4a–d** by dye-sensitized photo-oxygenation. Simply mixing the 1,2-dioxetanes with excess aldehyde, here exemplified by **5a** and acetaldehyde, in CH_2Cl_2 solution containing a catalytic amount of *Amberlyst-15* afforded the 1,2,4-trioxanes **7** and **8** *(Scheme 2)*. The sole by-product was adamantanone **15**. The trioxanes were usually formed as pairs of epimers with the *erythro* series (*e.g.* **7**) strongly predominating *(Table)*. Structures were assigned by means of ^{1}H- and ^{13}C-NMR spectroscopy and by comparison with previously established structures [5–7].

The 1,2-dioxetanes **5a–b** reacted efficiently with acetaldehyde, but *p*-chloro- and *p*-methoxyphenoxy-substituted dioxetanes **5b** and **5d** gave the highest yields (72–75%) of trioxanes **7b, 8b** and **7d, 8d**. Trioxane formation also occurs with other aldehydes, such as propionaldehyde, *p*-chloro- and *p*-nitrobenzaldehyde. However, the yields were considerably lower (17–34%), even with otherwise effective dioxetane partners such as the *p*-chlorophenoxy derivative **5b**.

Scheme 2



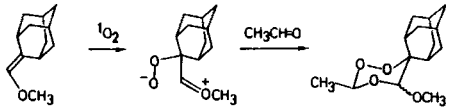
Discussion. – The results are best interpreted in terms of the intermediacy of the β-hydroperoxy phenoxonium cation **6** formed by protonation of the dioxetane **5**. It can be assumed that **6** is either sufficiently reactive or long-lived to be intercepted by aldehyde. Nucleophilic attack by the hydroperoxy group is relayed through the carbonyl function to cancel the charge on the positive center, thereby creating the trioxane ring.

The incoming aldehyde molecule can adopt either a *syn* or an *anti* orientation with respect to the phenoxonium entity. Preference for one orientation over the other is probably dictated by steric factors associated with the construction of the chair conformation of the six-membered ring.

The present reaction finds mechanistic parallels with the protonation of certain *endo*-1,4-peroxides [5], the behaviour of trimethylsilyl α-trimethylsilylperoxy carboxylates [6], and the photo-oxygenation of enol ethers [7]. In all these cases, the critical reactive intermediate possesses the same structural features as **6**, namely, a peroxy grouping adjacent to a real or formal cationic center.

However, for the last-mentioned reaction, a subtle, yet important, difference exists. For example, the photo-oxygenation of 2-methoxymethylideneadamantane **16** yields a zwitterionic peroxide **17** which can be captured by acetaldehyde to produce trioxanes **18** [7] *(Scheme 3)*. In contrast, the photo-oxygenation of the phenoxy derivatives **4a, b** and **d**, using rose bengal as sensitizer, in excess acetaldehyde, gave solely the corresponding dioxetanes **5** together with some cleavage to **15**, despite the presumed intermediacy of the analogous zwitterion. Thus, traces of acid may be necessary, although hitherto assumed to be unimportant [7], for the formation of trioxanes from enol ethers.

Scheme 3



16 **17** **18**

Two other properties also seem to play a role; one is the inherent propensity of the dioxetane to undergo scission to adamantanone **15**. The other is the electrophilicity of the carbonyl partner. Both properties, if great and poor, respectively, will diminish the yield of trioxanes.

The present findings portend similar reactivity of allylic hydroperoxides towards aldehydes; such experiments are under study and will be reported elsewhere.

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Experimental Part

General. Thin layer chromatography (TLC): silica gel $60F_{254}$ *Merck*. Prep. layer chromatography: silica gel $60F_{254}$ (thickness 2 mm). All solvents were analytical grade *Merck*. Physical constants and spectra were determined using the following instrumentation. Melting points (m.p.): *Reichert* hot-stage microscope (uncorrected). IR spectra: *Perkin-Elmer 681* spectrometer. ^{1}H-NMR spectra (chemical shifts in ppm relative to internal TMS (= 0 ppm), coupling constants J in Hz): *Varian XL 100* spectrometer or *Bruker WH 360* spectrometer. Mass spectra: *Varian CH-4* instrument. Elemental analyses were carried out by Drs. *H.* and *K. Eder*, Service de Microchimie, Institut de Chimie Pharmaceutique, University of Geneva.

Preparation of Phenoxymethylideneadamantanes **4a–d**. The enol ethers **4a–d** were prepared from 2-adamantanone and the appropriate α-phenoxyacetic acid [8]. The yields cited below are based on adamantanone.

2-(Phenoxymethylidene)adamantane[1]) (**4a**). Yield 40%, m.p. 41–42° ([8]: 39°). ^{1}H-NMR (100 MHz, $CDCl_3$): 7.5 – 7.2 (*m*, 2H); 7.2 – 6.9 (*m*, 3H); 6.22 (*s*, 1H); 3.2 – 3.0 (*m*, 1H), 2.55 – 2.35 (*m*, 1H); 2.2 – 1.6 (*m*, 12H).

2-[(4-Chlorophenoxy)methylidene]adamantane[1]) (**4b**). Yield 25%, m.p. 44–44.5°. IR (CCl_4): 1680*w* (C=C). ^{1}H-NMR (100 MHz, $CDCl_3$): 7.35–7.15 (*m*, 2H); 7.1 – 6.8 (*m*, 2H); 6.17 (*s*, 1H); 3.08 (*m*, 1H); 2.45 (*m*, 1H); 2.1 – 1.7 (*m*, 12H). MS: 276 (6, $M^+ + 2$), 274 (20, M^+), 217 (4), 147 (12), 128 (6), 119 (16), 111 (9), 105 (45), 91 (100).

2-[(4-Methylphenoxy)methylidene]adamantane[1]) (**4c**). Yield 40%, m.p. 53–54°. IR (NaCl): 1685*m* (C=C). ^{1}H-NMR (360 MHz, $CDCl_3$): 7.09 (*d*, *J* = 8, 2H); 6.90 (*d*, *J* = 8, 2H); 6.16 (*s*, 1H); 3.09 (br. *s*, 1H); 2.42 (br. *s*, 1H); 2.29 (*s*, 3H); 2.05 – 1.75 (complex *m*, 12H). MS: 254 (100, M^+), 197 (8), 147 (17), 105 (17), 91 (33).

2-[(4-Methoxyphenoxy)methylidene]adamantane[1]) (**4d**). Yield 59%, m.p. 55–56° (recrystallized from hexane). IR (CCl_4): 1685*m* (C=C). ^{1}H-NMR (360 MHz, $CDCl_3$): 6.94 (*d*, *J* = 8, 2H); 6.84 (*d*, *J* = 8, 2H); 6.15 (*s*, 1H); 3.79 (*s*, 3H); 3.12 (br. *s*, 1H); 2.43 (br. *s*, 1H); and 2.05–1.75 (complex *m*, 12H). MS: 270 (100, M^+), 213 (5), 147 (11), 124 (28), 105 (17), 91 (29).

Preparation of 1,2-Dioxetanes **5a–5d**. 1.0–1.5 mmol of the enol ether (**4**) in 10 ml of dry THF was irradiated with a 500-W high-pressure Na-lamp under a continuous stream of O_2 using rose bengal (RB, 15 mg) as sensitizer at –78°. The progress of the reaction was checked by TLC (CH_2Cl_2). Usually 3–4 h were required for completion. The 1,2-dioxetane was isolated by CC (silica gel) at r.t. (CH_2Cl_2 hexane).

Tricyclo[3.3.1.1^{3,7}]decane-2-spiro-3'-(4-phenoxy-1,2-dioxetane) (**5a**). Yield 75%, m.p. 71–72° (recrystallized from pentane) ([9]: 85–87.5°). R_f 0.63 (CH_2Cl_2, silica gel). ^{1}H-NMR (100 MHz, $CDCl_3$): 7.5 – 6.8 (*m*, 5H); 6.07 (*s*, 1H); 3.1 – 2.9 (*m*, 1H); 2.8 – 2.6 (*m*, 1H); 2.2 – 1.4 (*m*, 12H).

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[1]) The IUPAC name for 'adamantane' is *tricyclo[3.3.1.1^{3,7}]decane*.

*Tricyclo[3.3.1.1^{3,7}]decane-2-spiro-3'-[4-(*p*-chlorophenoxy)-1,2-dioxetane]* (**5b**). Yield 66%, m.p. 93,5–94.5° (recrystallized from hexane CH_2Cl_2). R_f 0.69 (CH_2Cl_2, silica gel). ^{1}H-NMR (100 MHz, $CDCl_3$): 7.4 – 7.0 (*m*, 2H); 6.9 – 6.6 (*m*, 2H); 5.99 (*s*, 1H); 2.92 (*m*, 1H); 2.67 (*m*, 1H); 2.2 – 1.4 (*m*, 12H). ^{13}C-NMR (90.6 MHz, $CDCl_3$): Two dioxetane C-atoms at 107.7 (*d*) and 93.0 (*s*). MS: No molecular peak, 274 (0.4), 274 (1.2), 156 (24), 150 (98), 128 (100).

$C_{17}H_{19}ClO_3$ (306.789) Calc. C 66.56 H 6.24 Cl 11.56% Found C 66.71 H 6.12 Cl 11.41%

*Tricyclo[3.3.1.1^{3,7}]decane-2-spiro-3'-[4-(*p*-tolyloxy)-1,2-dioxetane]* (**5c**). Yield 31%, m.p. 63–63.5° (recrystallized from hexane). R_f 0.64 (CH_2Cl_2, silica gel). ^{1}H-NMR (360 MHz, $CDCl_3$): 7.08 (*d*, *J* = 8, 2H); 6.76 (*d*, *J* = 8, 2H); 5.99 (*s*, 1H); 2.95 (br. *s*, 1H); 2.67 (br. *s*, 1H); 2.31 (*s*, 3H); 2.05 – 1.6 (complex *m*, 12H). MS: 286 (0.1, M^+), 276 (0.2, $M^+ - 16$), 254 (0.2, $M^+ - 32$), 150 (100), 136 (41), 108 (64), 107 (66).

$C_{18}H_{22}O_3$ (286.371) Calc. C 75.50 H 7.74% Found C 75.72 H 7.60%

*Tricyclo[3.3.1.1^{3,7}]decane-2-spiro-3'-[4-(*p*-methoxyphenoxy)-1,2-dioxetane]* (**5d**). Yield 55%, m.p. 75–76° (recrystallized from hexane CH_2Cl_2). R_f = 0.50 (CH_2Cl_2, silica gel). ^{1}H-NMR (360 MHz, $CDCl_3$): 6.83 (*s*, 4H); 3.78 (*s*, 3H); 2.96 (br. *s*, 1H); 2.67 (br. *s*, 1H); 2.1 – 1.55 (complex *m*, 12H). ^{13}C-NMR (90.6 MHz, $CDCl_3$): Two dioxetane C-atoms at 108.5 (*d*) and 93.0 (*s*). MS: 302 (0.2, M^+), 286 (0.7, $M^+ - 16$), 270 (3, $M^+ - 32$), 179 (8), 151 (26), 150 (26), 124 (100), 109 (55).

$C_{18}H_{22}O_4$ (302.370) Calc. C 71.50 H 7.33% Found C 71.50 H 7.15%

General Procedure for the Synthesis of 1,2,4-Trioxanes. A mixture of 1,2-dioxetane (0.42 – 0.3 mmol), excess aldehyde, *Amberlyst-15* (*ca.* 250 mg) was stirred overnight in CH_2Cl_2 (5 ml) at 25°. After removal of resin and solvent by filtration and evaporation, excess aldehyde was evaporated under high vacuum (*p*-chlorobenzaldehyde was removed by sublimation at 40°). The residue was purified by preparative layer chromatography. 1,2,4-Trioxanes were isolated as epimeric mixtures except when *p*-chlorobenzaldehyde was used. All compounds were formed as oils, except as noted. The data below refer to *erythro/threo*-mixtures which were not separated. However, the ratios of diastereomers are estimated from the intensities of characteristic NMR signals. The yields and ratios are shown in the *Table*.

erythro/threo-*Tricyclo[3.3.1.1^{3,7}]decane-2-spiro-6'-(3-methyl-5-phenoxy-1,2,4-trioxane)* (**7a**/**8a**). R_f 0.62 (CH_2Cl_2, silica gel). ^{1}H-NMR (360 MHz, $CDCl_3$): 7.4 – 7.3 (*m*, 2H); 7.2 – 7.0 (*m*, 3H); 5.87 (*q*, *J* = 5.5, *H*–C–CH_3, *threo*); 5.56 (*q*, *J* = 5, *H*–C–CH_3, *erythro*); 5.74 (*s*, H–C–O, *threo*); 5.41 (*s*, H–C–O, *erythro*); 2.85 – 1.4 (*m*, adamantyl); 1.48 (*d*, *J* = 5.5, CH_3, *erythro*); 1.29 (*d*, *J* = 5.5, *threo*). MS: 316 (4, M^+), 179 (11), 164 (25), 151 (13), 150 (15), 121 (12), 120 (100).

$C_{19}H_{24}O_4$ (316.397) Calc. C 72.13 H 7.65% Found C 71.94 H 7.68%

erythro/threo-*Tricyclo[3.3.1.1^{3,7}]decane-2-spiro-6'-[5-(*p*-chlorophenoxy)-3-methyl-1,2,4-trioxane]* (**7b**/**8b**). R_f 0.68 (CH_2Cl_2, silica gel). ^{1}H-NMR (360 MHz, $CDCl_3$): 7.35 – 7.2 (*m*, 2H); 7.1 – 6.95 (*m*, 2H); 5.80 (*q*, *J* = 5, *H*–C–CH_3, *threo*); 5.51 (*q*, *J* = 5, *H*–C–CH_3, *erythro*); 5.66 (*s*, H–C–O, *threo*); 5.34 (*s*, H–C–O, *erythro*);

Table. *Reaction of 1,2-Dioxetanes* **5** *with Aldehydes to Give Diastereomeric Pairs of 1,2,4-Trioxanes* **7**–**14**

1,2-Dioxetane	Aldehyde	1,2,4-Trioxetane	Yield %	*erythro/threo* Ratio
5a	CH_3CHO	**7a**, **8a**	47	9:5
5b		**7b**, **8b**	72	3:1
5c		**7c**, **8c**	45	3:2
5d		**7d**, **8d**	75	2:1
5a	*p*-ClC_6H_4CHO	**9a**, (**10a**)[a])	27	∞
5b		**9b**, (**10b**)[a])	17	∞
5a	*p*-$O_2NC_6H_4CHO$	**11a**, **12a**	17	3:1
5a	CH_3CH_2CHO	**13a**, **14a**	34	4:1

[a]) None of the *threo*-isomers **10a** and **10b** was formed in any detectable quantity.

2.8 – 1.4 (*m*, adamantyl); 1.45 (*d*, *J* = 5, CH_3, *erythro*); 1.27 (*d*, *J* = 5, CH_3, *threo*). MS: no molecular peak, 150 (37), 128 (37), 88 (63), 86 (100).

$C_{19}H_{23}ClO_4$ (350.842) Calc. C 65.05 H 6.61 Cl 10.11% Found C 65.26 H 6.70 Cl 9.97%

erythro/threo-*Tricyclo[3.3.1.1^{3,7}]decane-2-spiro-6'-[3-methyl-5-(*p*-tolyloxy)-1,2,4-trioxane]* (**7c**/**8c**). R_f 0.62 (silical gel, CH_2Cl_2). ^{1}H-NMR (360 MHz, $CDCl_3$): 7.10 (*d*, *J* = 8, 2H); 7.00–6.95 (2*d*, *J* = 8, 2H); 5.84 (*q*, *J* = 5.5, $H-C-CH_3$, *threo*); 5.52 (*q*, *J* = 5.5, $H-C-CH_3$, *erythro*); 5.65 (*s*, $H-C-OC_6H_4$, *threo*); 5.33 (*s*, $H-C-OC_6H_4$, *erythro*); 2.30 (*s*, $CH_3C_6H_4$); 2.8 – 1.45 (*m*, adamantyl); 1.43 (*d*, *J* = 5.5, CH_3CH, *erythro*); 1.26 (*d*, *J* = 5.5, CH_3CH, *threo*). MS: 330 (3, M^+), 270 (6), 254 (4), 241 (3), 179 (16), 151 (34), 150 (30), 109 (100), 108 (48).

$C_{20}H_{26}O_4$ (330.424) Calc. C 72.70 H 7.93% Found C 72.91 H 7.75%

erythro/threo-*Tricyclo[3.3.1.1^{3,7}]decane-2-spiro-6'-[5-(*p*-methoxyphenoxy)-3-methyl-1,2,4-trioxane]* (**7d**/**8d**). R_f 0.58 (silica gel, CH_2Cl_2). ^{1}H-NMR (360 MHz, $CDCl_3$): 7.04 (*d*, *J* = 7); 7.01 (*d*, *J* = 8, 2H); 6.85 (*d*, *J* = 8, 2H); 5.86 (*q*, *J* = 5.5, $H-C-CH_3$, *threo*); 5.52 (*q*, *J* = 5.5, $H-C-CH_3$, *erythro*); 5.59 (*s*, $H-C-OC_6H_4$, *threo*); 5.25 (*s*, $H-C-OC_6H_4$, *erythro*); 3.78 (*s*, CH_3O); 2.8 – 1.45 (*m*, adamantyl); 1.45 (*d*, *J* = 5.5, CH_3CH, *erythro*); 1.27 (*d*, *J* = 5.5, CH_3CH, *threo*). MS: 346 (3, M^+), 179 (12), 151 (30), 150 (27), 124 (100), 109 (37).

$C_{20}H_{26}O_5$ (346.423) Calc. C 69.34 H 7.57% Found C 69.15 H 7.52%

erythro-*Tricyclo[3.3.1.1^{3,7}]decane-2-spiro-6'-[3-(*p*-chlorophenyl)-5-phenoxy-1,2,4-trioxane]* (**9a**). M.p. 154–155° (recrystallized from hexane). ^{1}H-NMR (360 MHz, $CDCl_3$): 7.45–6.95 (*m*, 10H); 6.58 (*s*, 1H); 5.84 (*s*, 1H); 2.83 (br. *s*, 1H); 2.30 (*m*, 2H); 2.12 (br. *d*, *J* = 12, 1H); 2.0 – 1.45 (*m*, 10H). MS: 414 (0.2, $M^+ + 2$), 412 (0.7, M^+), 383 (0.6), 321 (4), 319 (11), 240 (16), 179 (51), 161 (19), 151 (48), 150 (28), 141 (33), 140 (25), 139 (100). (The peaks $M^+ + 2$ and M^+ were obtained by CI-MS).

$C_{24}H_{25}ClO_4$ (412.913) Calc. C 69.81 H 6.10 Cl 8.59% Found C 69.93 H 6.31 Cl 8.78%

erythro-*Tricyclo[3.3.1.1^{3,7}]decane-2-spiro-6'-[5-(*p*-chlorophenoxy)-3-(*p*-chlorophenyl)-1,2,4-trioxane]* (**9b**). M.p. 143° (decomp.). ^{1}H-NMR (360 MHz, $CDCl_3$): 7.40 (*d*, *J* = 8.5, 2H); 7.33 (*d*, *J* = 8.5, 2H); 7.23 (*d*, *J* = 8.5, 2H); 7.07 (*d*, *J* = 8.5, 2H); 6.55 (*s*, 1H); 5.81 (*s*, 1H); 2.85 (*m*, 1H); 2.35 – 1.45 (*m*, 13H). MS: no molecular peak, 319 (5, $M^+ - C_6H_4ClO$), 179 (9), 161 (8), 151 (18), 139 (36), 128 (55), 111 (22), 91 (100), 79 (85).

$C_{24}H_{24}Cl_2O_4$ (447.358) Calc. C 64.44 H 5.41 Cl 15.58% Found C 64.45 H 5.58 Cl 15.74%

erythro/threo-*Tricyclo[3.3.1.1^{3,7}]decane-2-spiro-6'-[3-(*p*-nitrophenyl)-5-phenoxy-1,2,4-trioxane]* (**11a**/**12a**). R_f 0.73 (CH_2Cl_2, silica gel). ^{1}H-NMR (360 MHz, $CDCl_3$): 8.18 (*d*, *J* = 9); 7.70 (*d*, *J* = 9, $C_6H_4-NO_2$, *erythro*); 8.27 (*d*, *J* = 9); 7.71 (*d*, *J* = 9, $C_6H_4-NO_2$, *threo*); 7.4 – 6.95 (*m*, C_6H_5O); 6.77 (*s*, H–C–O, *threo*); 6.43 (*s*, H–C–O, *erythro*); 5.96 (*s*, H–C–O, *threo*); 5.34 (*s*, H–C–O, *erythro*); 2.95 – 1.6 (*m*, adamantyl). MS: 423 (3, M^+), 330 (3), 300 (7), 240 (8), 179 (25), 163 (10), 162 (44), 161 (12), 151 (51), 150 (100).

$C_{24}H_{25}NO_6$ (423.465) Calc. C 68.07 H 5.95 N 3.31% Found C 68.30 H 6.20 N 3.04%

erythro/threo-*Tricyclo[3.3.1.1^{3,7}]decane-2-spiro-6'-(3-ethyl-5-phenoxy-1,2,4-trioxane)* (**13a**/**14a**). R_f 0.47 (CH_2Cl_2 hexane 3:2, silica gel). ^{1}H-NMR (360 MHz, $CDCl_3$): 7.4 – 7.0 (*m*, C_6H_5); 5.73 (*s*, H–C–O, *threo*); 5.40 (*s*, H–C–O *erythro*); 5.66 (*t*, *J* = 5.5, H–C–O, *threo*); 5.31 (*t*, *J* = 5.5, H–C–O, *erythro*); 2.81 – 1.5 (*m*, adamantyl, CH_2); 0.98 (*t*, *J* = 7.5, CH_3, *erythro*); 0.94 (*t*, *J* = 7.5, CH_3, *threo*). MS: no parent peak, 250 (5), 175 (10), 158 (7), 157 (76), 156 (21), 151 (14), 150 (100).

$C_{20}H_{26}O_4$ (330.424) Calc. C 72.70 H 7.93% Found C 72.63 H 7.99%

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