

**SELECTIVITY AND CHARGE TRANSFER IN PHOTOREACTIONS
OF DONOR-ACCEPTOR SYSTEMS
XI: STEREOSELECTIVITIES IN META
PHOTOCYCLOADDITIONS OF PHENOL ETHERS TO OLEFINS***

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Summary

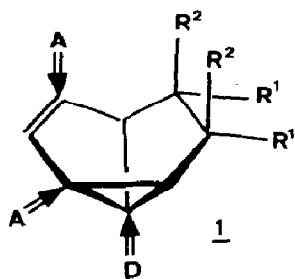
The stereoselectivity of photochemical meta cycloadditions of cyclic olefins to anisole and trimethylsiloxybenzene changes in favour of the exo isomer with the silyl ether despite more steric hindrance. This finding indicates secondary bonding interactions in polar intermediates which depend on substitution by methoxy or siloxy.

1. Introduction

Different mechanisms have been proposed for the meta photocycloaddition of arenes to olefins with the formation of **1** since its discovery nearly two decades ago [2]. The mechanism which currently fits all the experimental evidence and which is most favoured involves an exciplex intermediate [1 - 9]. Collapse of this exciplex **2** forms another type of intermediate, the meta-bonded species **3** [1, 5, 7, 9]. The dipolar character of **3** may depend on the stabilization by electron donor and/or acceptor substituents, which further determine the regiochemistry of **1** [1, 8, 10 - 13]. For convenience, these dipolar intermediates are represented as "zwitterions". Moreover, both the photoinduced charge transfer in the exciplex **2** [8] and the charge separation in the "zwitterion" **3** [1, 5, 6, 8, 11, 12] may influence the stereochemistry of the metal adduct **1**. For example, endo stereoselectivity is observed in most cycloadditions with alkenes such as cyclopentene [13, 14 - 16] and cyclo-octene [10], whereas 1,3-dioxoles add predominantly exo to arenes [5, 8, 11, 12, 17]. These effects have been rationalized

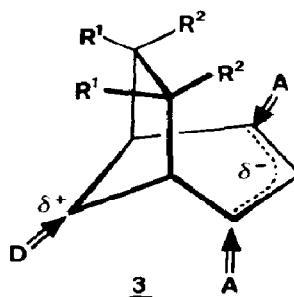
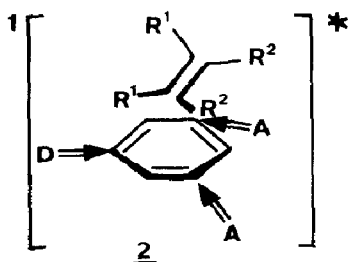
*For part X see ref. 1.

on the basis of secondary orbital interactions in the exciplex state for simple alkenes by Houk [18] and Bryce-Smith *et al.* [10] and for enol ethers and esters, *e.g.* vinylene carbonate, by ourselves [5, 6, 8, 11, 12, 17].



D = Donor Substituent

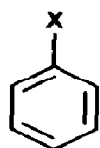
A = Acceptor Substituent



We now report the results of our investigations of meta cycloadditions of the phenol ethers 4a and 4b to cyclopentene 5a and 1,3-dioxole derivatives 5b and 5c which provide more information about the charge transfer-selectivity relationship.

2. Results

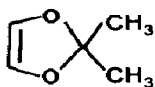
Irradiations at 254 nm (Grüntzel 160 W photoreactor) of solutions in cyclohexane (for 5a and 5b) or dioxane (for 5c) which contain the phenol ether 4a or 4b, respectively, and one of the olefins resulted in formation of the products 6 - 15. The concentrations were 0.3 M arene and 0.6 M olefin. The irradiations were stopped at a maximum of 50% conversion (maximum time, 40 h). In general the chemical yields of the product mixtures were 50% - 60% according to a nuclear magnetic resonance (NMR) analysis. After isolation of the pure components either by distillation (6b, 9b and 10b) and/or by high performance liquid chromatography (HPLC) the yields decrease by up to 30%. This is caused by the lability of the products under thermal and liquid chromatographic conditions, which especially concern products from 4b. In particular, the products from 4a and 5c, from 4b and 5b, and from 4b and 5c were isolated by means of HPLC using a silicon 60 column and mixtures containing a maximum of 60% ethyl acetate in hexane as eluent.



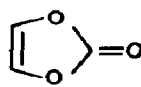
4a
4b



5a



5b

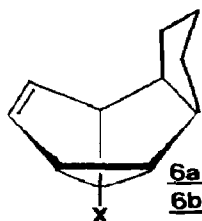


5c

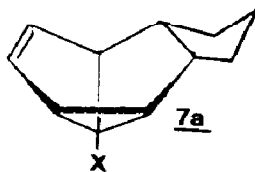
4, 6 - 13:

a, X ≡ OCH₃

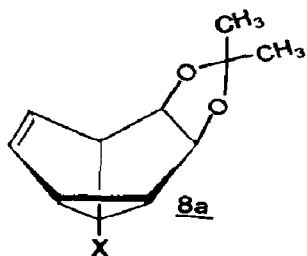
b, X ≡ OSi(CH₃)₃



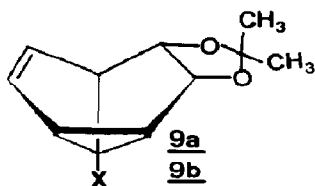
6a
6b



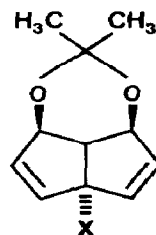
7a



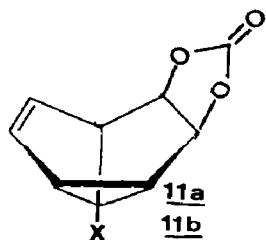
8a



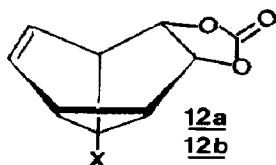
9a
9b



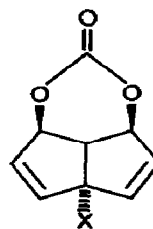
10b



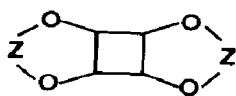
11a
11b



12a
12b



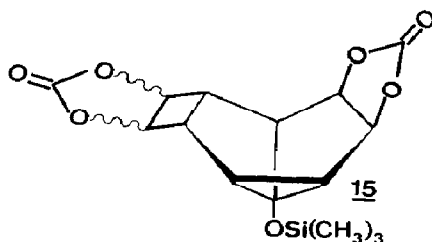
13a
13b



14

a, Z ≡ C(CH₃)₂

b, Z ≡ C=O



15
OSi(CH₃)₃

11a and 12a have already been described by Osselton *et al.* [19]. In addition to these meta adducts we have found the bicyclo[3.3.0]octa-2,7-diene derivatives 13a in 3% yield besides some 16% of ortho adducts. The yield of ortho adducts depends on the irradiation time due to photochemical consecutive reactions. Similar products, 10b in 10% and 13b in 6% yield,

TABLE 1

Ratios of endo and exo meta cycloadditions of anisole 4a and trimethylsilylphenyl ether 4b to cyclopentene 5a, 2,2-dimethyl-1,3-dioxole 5b and vinylene carbonate 5c in cyclohexane (maximum conversion, 20%)

Olefin	Endo:exo ratio	
	4a	4b
5a	9.3:1 ^a	Greater than 9:1 ^b
5b	1:3.2 ^c	Less than 1:9.3 ^d
5c	2.0:1 ^e	1.3:1 ^f

^aRef. 14.

^bAt least two side-products in less than 20% yield (1.4:1); dimers of 5a, less than 10%.

^cRef. 11.

^d10b:9b, at least two further side-products in less than 15% yield (2:1); 14a, about 10%.

^eIn dioxane, (11a + 13a):12a, at least two further side-products in about 16% yield (1:1); see also ref. 19.

^fIn dioxane, (11b + 13b + 15):12b, at least three further side-products in less than 25% yield; 14b, less than 10%.

which probably result from a rearrangement of the endo meta adducts [20] have been isolated from photoreactions with 4b. It should be noted that these products occur even in the reaction mixtures. Contrary to that, a similar rearranged product from benzene and 5c has only been formed on heating to 150 °C [20]. We are currently studying the conditions for the formation of bicyclo[3.3.0]octa-2,7-dienes from the endo meta adducts.

The stereoselectivity (endo:exo ratio) of the meta cycloadditions depends strongly on the starting materials (Table 1). In general, cyclopentene 5a and vinylene carbonate 5c preferentially form endo-configured meta adducts whereas the dioxole 5b shows the reverse behaviour. Moreover, the following points are noteworthy.

(1) Both 4a and 4b form endo meta cycloadducts with 5a highly preferentially.

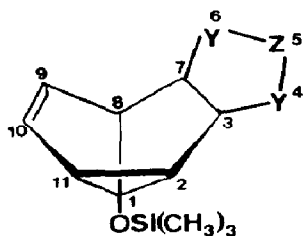
(2) In general the trimethylsilyl phenyl ether 4b yields more exo isomers than anisole 4a in meta cycloadditions with 5b and 5c despite more steric hindrance caused by the bulky trimethylsilyl group.

The ¹H and ¹³C NMR spectroscopic data for the new meta adducts 6b, 9b, 11b and 12b are summarized in Tables 2 and 3. Both tables show the typical chemical shifts and coupling constants which are expected for exo and endo meta adducts with methoxy or siloxy at position 1 [5, 7, 11 - 14, 17, 19, 21]. The meta adducts 11a and 12a have been independently described by Osselton *et al.* [19] and our data are actually identical with their results. 6a and 7a [14, 21] and 8a and 9a [11] have already been reported elsewhere. Tables 4 and 5 show the NMR data for the tetrahydropentalene derivatives 10b, 13a and 13b. Mass spectroscopy (MS) and NMR data confirm the structure of the 1:2 adduct 15 between 4b and 5c.

TABLE 2

^1H NMR spectroscopic data (δ_{H} (ppm) and J (Hz)) for **6b**, **9b** (in CDCl_3) and **11b**, **12b** (in C_6D_6)

^1H	6b	9b	11b	12b
$\text{OSi}(\text{CH}_3)_3$	0.05 (s)	0.10 (s)	0.10 (s)	0.10 (s)
2	1.85 (m)	2.10 (m)	2.10 (m)	2.05 (m)
3	2.9 (m)	4.13 (d) ^c	4.83 (m)	4.10 (d) ⁱ
4 - 6	1.2 - 1.8 (m)	1.26 (s) ^b 1.53 (s) ^b	—	—
7	3.3 (m)	4.23 (d) ^c	4.83 (m)	4.22 (d) ⁱ
8	2.86 (dm) ^a	3.30 (d) ^d	3.23 (m)	3.27 (d) ^j
9	5.55 (m)	5.42 (dd) ^{d,e}	5.48 (dm) ^g	5.05 (m)
10	5.55 (m)	5.60 (dd) ^{e,f}	5.67 (dm) ^g	5.33 (dd) ^{k,1}
11	1.85 (m)	2.10 (m)	2.10 (m)	2.05 (m)



$$^a J_{7,8} = 7.$$

$$^b \text{Y} \equiv \text{O}, \text{Z} \equiv \text{C}(\text{CH}_3)_2.$$

$$^c J_{3,7} = 4.2.$$

$$^d J_{8,9} = 2.7.$$

$$^e J_{9,10} = 5.4.$$

$$^f J_{10,11} = 2.1.$$

$$^g J_{9,10} = 5.7.$$

$$^h J_{10,11} = 2.2.$$

$$^i J_{3,7} = 5.0.$$

$$^j J_{8,9} = 2.7.$$

$$^k J_{9,10} = 5.7.$$

$$^l J_{10,11} = 2.2.$$

TABLE 3

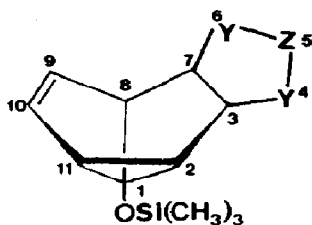
^{13}C NMR spectroscopic data (δ_{C} (ppm)) for **6b**, **9b**, **11b** and **12b** in CDCl_3

^{13}C	6b	9b	11b	12b
$\text{OSi}(\text{CH}_3)_3$	0.42	0.72	0.00	0.07
1	89.89	83.05	84.63	81.61
2	37.68	36.24	35.26	36.15
3	48.68	81.45	83.99	81.18
4	26.25 ^a	—	—	—
5	29.08 ^a	110.77 ^e	154.93	154.48
6	29.64 ^a	—	—	—
7	59.19 ^b	88.57	85.86	87.28
8	59.26 ^b	58.39	57.83	57.78
9	129.33 ^c	128.90 ^d	129.98	127.68

(continued)

TABLE 3 (continued)

^{13}C	<i>6b</i>	<i>9b</i>	<i>11b</i>	<i>12b</i>
10	134.06 ^c	129.01 ^d	132.01	130.20
11	38.50	40.84	37.72	38.50



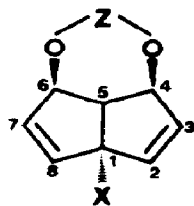
^{a-d} Assignment may be reversed.

^e $\delta(\text{CH}_3) = 26.13$ and 27.44 .

TABLE 4

^1H NMR spectroscopic data (δ_{H} (ppm) and J (Hz)) for *10b*, *13a* and *13b* in CDCl_3

^1H	<i>10b</i>	<i>13a</i>	<i>13b</i> ^f
X	0.60 (s)	3.20 (s)	0.10 (s)
2/8	6.07 (dd) ^{a,b}	6.27 (dd) ^{b,e}	5.93 (dd) ^{b,e}
3/7	5.92 (dd) ^{a,c}	6.00 (dd) ^{c,e}	5.53 (dd) ^{c,e}
4/6	5.12 (ddd) ^{b-d}	5.53 (ddd) ^{b-d}	5.05 (ddd) ^{b-d}
5	2.58 (t) ^d	3.11 (t) ^d	2.63 (t) ^d
Z	1.33 (s), 1.45 (s)	—	—



^a $J_{2,3} = J_{7,8} = 5.4$. ^b $J_{2,4} = J_{6,8} = 1.0$. ^c $J_{3,4} = J_{6,7} = 2.0$. ^d $J_{4,5} = J_{5,6} = 7.8$. ^e $J_{2,3} = J_{7,8} = 5.7$.
^f In C_6D_6 .

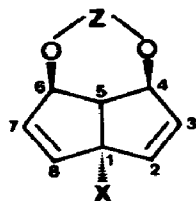
3. Discussion

The mode selectivities of these photocycloadditions are in accordance with those of other photoreactions between arenes and olefins and may be understood on the basis of a correlation with the free enthalpies of electron transfer [8]. Meta cycloaddition is the only observed reaction of the phenol ethers with cyclopentene which corresponds to $\Delta G > 1.75$ eV of electron

TABLE 5

¹³C NMR spectroscopic data (δ_C (ppm)) for 10b, 13a and 13b in CDCl₃

¹³ C	10b	13a	13b
X	1.93	52.39	1.34
1	96.64 ^a	102.62	— ^e
2/8	138.51 ^b	140.32 ^b	142.17 ^b
3/7	134.78 ^b	132.72 ^b	130.54 ^b
4/6	74.91	82.75	82.36
5	46.98	42.27	46.98
Z	99.14 ^{a,d}	149.21	— ^e

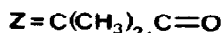
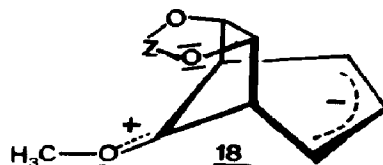
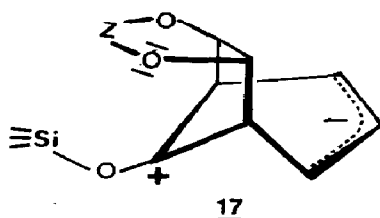
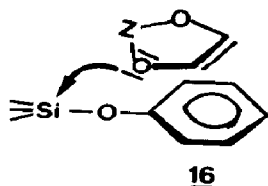
^{a-c} Assignment may be reversed.^d $\delta(\text{CH}_3) = 23.79$ and 29.39 .^e Signal too weak for detection.

transfer. Since the reduction potentials of 4a and 4b are not measurable [8] ΔG can only be estimated using eqn. (3) of ref. 8 for calculation of the values of the corresponding photoreactions with benzene: $\Delta G(\text{phenol ether}) > \Delta G(\text{benzene})$, if the arene acts as acceptor. The electrochemical redox potentials (*vs.* Ag/AgNO₃ electrode in acetonitrile) and the excitation energies of 4a and 4b do not differ significantly: $E_{1/2}^{\text{ox}}(4a) = 1.34$ V, $E_{1/2}^{\text{ox}}(4b) = 1.35$ V, $\Delta E_{\text{excit}}(4a) = 4.46$ eV, $\Delta E_{\text{excit}}(4b) = 4.54$ eV. For potentials of the other reactants see ref. 8. Formation of ortho cycloadducts is observed in photoreactions with 5b and 5c. (The yield of ortho adducts depends on the irradiation time due to photochemical consecutive reactions.) This again is in accordance with the thermodynamic data of electron transfer $\Delta G(4a/4b + 5b) > 0.63$ eV, $\Delta G(4a + 5c) = 0.34$ eV and $\Delta G(4b + 5c) = 0.27$ eV. It should be noted that in the latter two reactions the arenes act as electron acceptors [8].

The preferred formation of 1-substituted meta adducts can be easily understood by assuming dipolar intermediates of the type 3 with stabilizing ether groups at the positive centre. The high regioselectivity which is observed here further confirms the validity of the "exciplex-zwitterion mechanism" [11].

Differences in the endo:exo ratio in photoreactions within one column of Table 1 are obviously caused by different types of secondary orbital interactions with the olefins 5a - 5c. These interactions may be of an "intermolecular hyperconjugation type" as emphasized by Bryce-Smith *et al.* [10] (see also ref. 18) which favour the endo stereochemistry with alkenes such

as 5a. Another type may be due to interactions between the n orbitals of the oxygens of enol derivatives such as 5b and 5c and the arene part, which is further influenced by the direction of charge transfer (CT) [5, 8, 11, 12, 17]. However, the CT character of an exciplex involving either 4a or 4b should be similar owing to almost equal electrochemical redox potentials and excitation energies of the phenol ethers. As a consequence the observed stereochemical effect should be caused mainly by the influence of silicon in the exciplex and/or the "zwitterion" state. One possible explanation is shown in formula 16 with a stabilization of the exo geometry by $p \rightarrow d$



bonding in the exciplex despite its higher steric hindrance. This secondary bonding interaction could be due to the ability of silicon to expand its coordination [22] and should be effective even in a "zwitterionic" intermediate. Another explanation is also based on the overlap of oxygen 2p lone pairs with empty 3d orbitals of silicon, *i.e.* on the partial double-bond character of Si-O bonds [22]. Accordingly, a dipolar intermediate, which is substituted with siloxy rather than with methoxy, has more cationic character at position 1 (see 17 in comparison with 18). Consequently the exo configuration of the dioxolane ring is stabilized more efficiently by an interaction between the oxygen lone pairs and the cationic charge at position 1 in 17. An ether oxygen obviously supports these secondary interactions more than an ester oxygen and consequently 4b and 5b form almost exclusively the exo meta adduct 9b (see Table 1).

The occurrence of the tetrahydropentalene derivatives 10b, 13a and 13b is somewhat surprising since similar products have only been formed thermally by a rearrangement from endo meta adducts at 150 - 300 °C [20, 23]. The rearrangements have been rationalized in terms of a 1,5-sigmatropic shift and a 2'-vinylcyclopropylcyclobutane rearrangement. For 13a and 13b the experimental conditions indicate, however, that the rearrangements may proceed catalytically, *e.g.* they are caused by the acidic centres of the silica material which is used for chromatographic purposes. However, 10b occurs in the reaction mixture even before working-up procedures.

4. Experimental details

4.1. Chemicals and equipment

Commercially available anisole **4a** and cyclopentene **5a** were purified by distillation. Trimethylsilyl phenyl ether **4b** was synthesized from phenol and trimethylchlorosilane as described by Langer *et al.* [24]. 2,2-Dimethyl-1,3-dioxole **5b** and vinylene carbonate **5c** were synthesized according to Field [25] and Newman and Addor [26] respectively. For preparative procedures the solvents were purified by standard methods. In particular, peroxides were removed from dioxane. Spectrophotometric grade solvents (from Fluka) were used for analytical investigations such as small-scale irradiations and electrochemical measurements. In the latter case, spectrophotometric grade acetonitrile was further purified and the electrochemical redox potentials were measured by cyclic voltammetry as described previously [8]. A photoreactor from Gräntzel (Karlsruhe, 160 W low pressure mercury lamp, quartz filter) or a merry-go-round apparatus from Mangels (Bornheim/Reisdorf, TNN 15/32 lamp from Hanau) were used for preparative or analytical irradiations respectively.

IR spectra were recorded on a Perkin-Elmer 377 spectrometer. ^1H and ^{13}C NMR spectra were measured using a Varian EM 390 (90 MHz) and a Varian CFT 20 (20 MHz) spectrometer respectively. For NMR data see also Tables 2 - 5. Gas chromatographic analyses were performed on a Carlo-Erba Fractovap 2101 using OV 17, OV 101 and NPGS glass columns, all 5% - 10% on Chromosorb WAW DMCS 80/100 mesh. A Perkin-Elmer Ser. 3-LC-65 T and a Gilson 303 chromatograph were used for analytical and preparative liquid chromatographic separations respectively. In both cases Chromosorb silicon 60 columns and mixtures of 3% - 60% ethyl acetate in hexane were used as eluents.

4.2. Preparative photoreactions and product isolation

Solutions (120 ml) containing the arene (0.3 M) and the olefin (0.6 M) were irradiated under a nitrogen atmosphere up to a maximum of 50% conversion. Dioxane was used as solvent only with **5c** for reasons of solubility; all the other photoreactions were performed in cyclohexane. The irradiation time was 20 h (**5a**, **5b**) or 40 h (**5c**). All products show satisfactory micro-analytical data: carbon, $\pm 0.30\%$; hydrogen, $\pm 0.20\%$.

After removing the solvents by distillation at room temperature (reduced pressure) the products from **5a** and **5b** were distilled (**6b**, boiling point, 45°C at 0.001 Torr; **9b** and **10b**, boiling point, $56 - 57^\circ\text{C}$ at 0.03 Torr). **6b** was already pure for NMR analysis. **9b** and **10b** were separated by means of HPLC (3% ethyl acetate in hexane). In addition, isomeric side-products could be detected according to their gas chromatographic (GC)-MS data, which are typical for 1:1 cycloadducts (compare for example refs. 11, 12 and 27). Moreover, dimeric products from **5a** and **5b** were identified by comparison with the authentic samples, *i.e.* cyclobutanes and acyclic dimers from **5a** [28] and **14a** [27].

The products from 4a and 5c were isolated somewhat differently. After removing the solvents by distillation under reduced pressure at room temperature, the product mixture from 4a and 5c was filtered over silica gel (Woelm 32-100 mesh) using 60% ethyl acetate in hexane as eluent. This pre-purified mixture was then separated into its components by means of HPLC using the same eluent. 11a and 12a were identical with Cornelisse's endo and exo meta cycloadducts of 4a and 5c [19]. Under the above-mentioned conditions, 13a and two further 1:1 adducts were eluted at higher retention times.

The products from 4b and 5c were isolated as follows. After removing the solvent (see above) the remaining oil was extracted with diethyl ether. The insoluble solid compound was identified as the dimer 14b [29]. Thin-layer chromatographic analyses of the ether-soluble extract show separations into several components with 35% ethyl acetate in hexane as eluent. A separation by means of HPLC using the same eluent mixture leads to the isolation of 11b, 12b, 13b and a fraction with a higher retention time, which was composed of the 1:2 adduct (15 melting point, 113 °C (decomposition)); ¹H NMR (δ, CDCl₃) 0.17 (s, 9H, Si(CH₃)₃), 2.19 (m, 2H, H-2 and H-16), 3.13 (m, 3H, H-8, H-9 and H-15), 5.10 (m, 4H, H-3, H-7, H-10 and H-14); ¹H NMR (δ, C₆D₆) 0.12 (s, 9H, Si(CH₃)₃), 1.57 (dm, *J* = 10.2 Hz and Σ*J* = 6 Hz, 1H, H-2), 1.87 (d, *J* = 10.2 Hz, 1H, H-16), 2.67 (m, 3H, H-8, H-9 and H-15), 4.23 (m, 2H, H-3 and H-7), 4.56 (m, 2H, H-10 and H-14); ¹³C NMR (δ, CDCl₃) 0.44 (Si(CH₃)₃), 32.65 and 35.82 (C-2 and C-16), 44.41, 45.52 and 52.90 (C-8, C-9 and C-15), 72.58, 76.62, 81.86 and 83.14 (C-3, C-7, C-10 and C-14), 81.34 (C-1), 154.54 and 155.75 (C-5 and C-12).

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