264. Preference for Syn Ene Additions of $^1O_2$ to Trisubstituted, Acyclic Olefins

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(2.X.78)

Summary

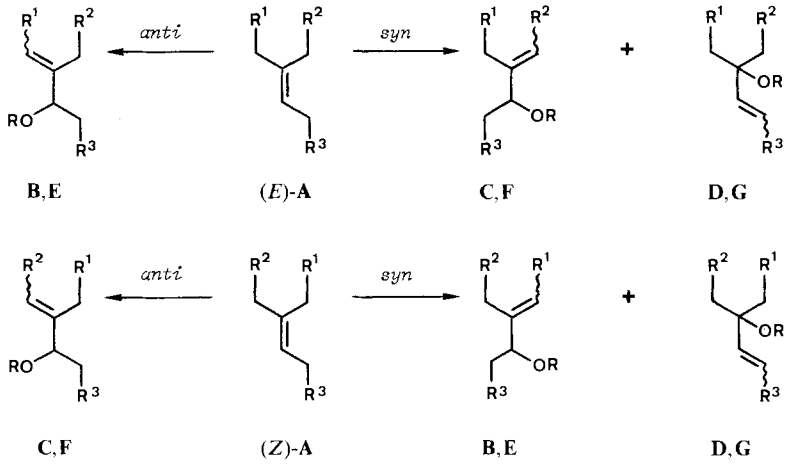
Dye-sensitized photooxygenations of 3 pairs of (*E*)/(*Z*) trisubstituted olefins were studied in order to establish the partitioning between the 3 possible ene additions. The (*E*)-isomers underwent only the 2 ene additions (> 95%) involving H-atom abstractions at the same, disubstituted side of the olefins, termed *syn* ene additions, with almost equal ease. The (*Z*)-isomers underwent mainly (85–90%) the *syn* ene additions, with the ones leading to the tertiary hydroperoxides distinctly favoured, and some (10–15%) ene additions at the monosubstituted side of the olefin, termed *anti* ene addition.

Trisubstituted, acyclic olefins of type **A** *(Scheme 1)* react with $^1O_2$ by ene additions only [1–4]. In principle, 3 additions involving H-atom abstractions from the 3 methylene groups can take place. The one involving H-atom abstraction from the lone methylene group leads to a tertiary hydroperoxide and those involving H-atom abstractions from the geminal methylene groups lead to secondary hydroperoxides. Tertiary and secondary hydroperoxides are formed in similar amounts [1–3] and it is usually assumed that both ene additions leading to secondary hydroperoxides take place, but in all reported work these could not ($R^1 = R^2$) [1–3] or were not ($R^1 \neq R^2$) distinguished in a systematic fashion [4b] [5] [6][1]).

We term the ene additions at the disubstituted side of the olefin **A** *syn* ene additions, and the ene addition at the monosubstituted side *anti* ene addition. Consider the ene additions to the geometrical isomers (*E*)-**A** and (*Z*)-**A** *(Scheme 1). Anti* ene additions give the secondary hydroperoxides **B** from (*E*)-**A** and **C** from (*Z*)-**A**. Conversely, *syn* ene additions give **C** from (*E*)-**A** and **B** from (*Z*)-**A**, and in addition the tertiary hydroperoxide **D** from either (*E*)- or (*Z*)-**A** (if $R^1 = R^2$ then (*E*)-**A** = (*Z*)-**A** and **B** = **C**).

[1]) $^1O_2$ has been found to react with the 6,7-double bond of (*E,E*)-α-farnesene to give the hydroperoxides resulting from the ene additions at the disubstituted side. The absence of the third hydroperoxide and the product distribution were not established [5]. The reaction of $^1O_2$ with (*E*)-4-methyloct-4-ene has been reported to give all 3 hydroperoxides. The two hydroperoxides derived from the $^1O_2$-addition at the disubstituted side of the double bond were the main products and formed in nearly equal amounts [6]. For related work with 2-cyclopropyl-but-2-enes, see [7].

Scheme 1. *The 3 possible ene-reactions of* $^1O_2$ *with* (E)-**A** *and* (Z)-**A**



B, **E** (*E*)-**A** **C**, **F** **D**, **G**

C, **F** (*Z*)-**A** **B**, **E** **D**, **G**

B, **C**, **D**: R = OH
E, **F**, **G**: R = H

A = 1 **E** = 4, **F** = 5, **G** = 6 $R^1 = -CH_3$, $R^2 = R^3 = H$

A = 2 **E** = 7, **F** = 8, **G** = 9 $R^1 = -(CH_2)_2C(CH_3)=CH_2$; $R^2 = H$; $R^3 = -(CH_2)_2CH_3$

A = 3 **E** = 10, **F** = 11, **G** = 12 $R^1 = -(CH_2)_2C(CH_3)=CH_2$; $R^2 = H$; $R^3 = -CH(CH_3)_2$

Combination of all current mechanistic hypotheses with steric considerations leads to the conclusion that the *anti* ene addition should be favoured over the individual *syn* additions. To our knowledge, there are no other theoretical or empirical guidelines. However [8] [9], (*E*)- and (*Z*)-caryophyllene react with $^1O_2$ mainly by *syn* ene additions, and the partitioning between the various *syn* addition modes is different. This could not be explained satisfactorily in terms of the steric and conformational peculiarities of the system alone and we hypothesized that this was perhaps the normal, previously unnoticed behaviour of trisubstituted olefins. We now report that the *syn* ene additions are preferred in acyclic analogues.

The pure (> 98%) (*E*)- and (*Z*)-isomers of **1**, **2** and **3** were subjected to standard dye-sensitized photooxygenation in solution up to near-complete conversion. Ene additions were the only significant reactions and the product distributions were practically independent of the degree of conversion[2]). The hydroperoxides **B**, **C**, and **D** were reduced by standard procedures to the alcohols **E**, **F**, and **G**, respectively *(Scheme 1)*. The identification of the products and the determination of the product

[2]) The product distributions during a run did not vary beyond ± 10% (relative error). This fact and the high yields of alcohols show that the hydroperoxides **B** did not undergo secondary oxygenation at the newly formed trisubstituted double bonds to a significant extent.

Table. *Dye-sensitized photooxygenations of the (E)/(Z) olefines* **1–3**

Substrate	Products and product distributions (in %)[a]			combined yields[b]	β-values[a]
A	E	F	G	%	[M]
(E)-	≤5	42	53	82	0.05
(Z)- **1**	12 **4**	15 **5**	73 **6**	78	0.06
(E)-	≤5	46	49	77	0.10
(Z)- **2**	18 **7**	10 **8**	72 **9**	75	0.13
(E)-	≤5	41	54	80	0.08
(Z)- **3**	14 **10**	10 **11**	76 **12**	75	0.11

[a]) See exper. part.
[b]) Distilled mixture of alcohols.

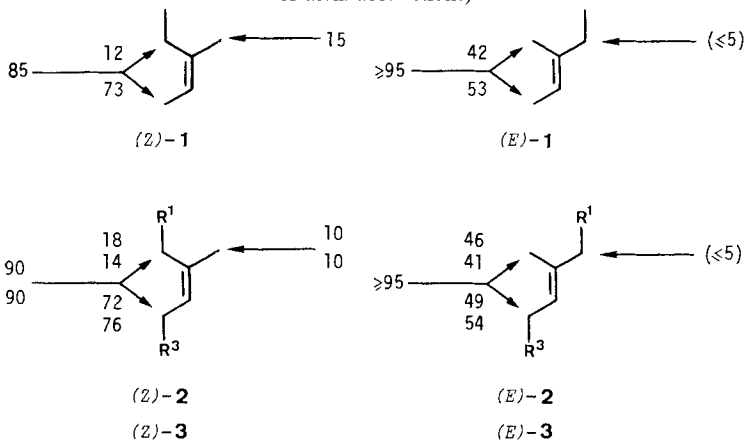
distributions were carried out at the level of the alcohols. The (*Z*)-isomers of the alcohols **7**, **9**, **10**, and **12** were not found. From (*E*)-**1** and (*Z*)-**1**, (*Z*)-**4**, which could not be identified with certainty, was probably also formed.

The alcohols were separated by a combination of distillation and preparative GC. and identified from their spectra and, in part, by comparison (spectra) with authentic samples. Products, product distributions, yields, and reactivities (β-values [10]) are collected in the *Table*. The partitioning between the ene reactions is also summarized in *Scheme 2*.

Within the (absolute) analytical error (5%, see exper. part), *the 3 (*E*)-isomers undergo only the 2* syn *ene additions*, with almost equal ease (the tertiary and secondary hydroperoxides are formed in *ca.* 1:1 ratios), and react somewhat more rapidly then the corresponding (*Z*)-isomers. *The 3 (*Z*)-isomers undergo mainly (85–90%) the 2* syn *ene additions*, of which those leading to the tertiary hydroperoxides are now distinctly favoured (the tertiary and secondary hydroperoxides are formed in ratios from 4:1 to 6:1), and to a minor extent (10–15%) *anti* ene addition.

These results show a clear preference for the *syn* ene additions of $^1O_2$, well beyond that expected on statistical grounds (see below) and contrary to what one would expect on steric grounds. The results are, however, somewhat ambiguous, for the following reasons: (1) H-atom abstractions at methyl and methylene groups compete, the intrinsic reactivities of these groups are probably not very different but

Scheme 2. *Partitioning* (in %) *between the 3 ene-reactions of* **1–3** (the arrows indicate the sites of the H-atom abstractions)



are not accurately known; (2) the statistical factors favour the H-atom abstraction at a methyl group over the H-atom abstraction at a methylene group. They also favour the *syn* additions over the *anti* additions; these factors must play a role but clearly do not suffice to explain our results.

For rigorous analyses, a 2-methylbut-2-ene is required isotopically labelled so that the reactions at the 3 methyl groups can be distinguished *(Scheme 1)*, and a derivative **A** substituted ($R^1 = R^3 =$ alkyl, $R^2 =$ analogue R^1 and R^3) or better, labelled ($R^1 = R^2 = R^3 = CH_2R$) so that the reactions at the 3 methylene groups can be distinguished. We are now undertaking these more demanding experiments.

We leave open the theory behind the new principle, but believe that knowledge of its existence will be useful in synthesis. Recently described orientational phenomena in the ene reactions of $^1O_2$ with enol ethers [7] [11] [12] and 3,3-dialkyl-substituted allyl alcohols [13] may be related.

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Experimental Part

(With the collaboration of *H. Pamingle*)

General. 60 MHz ^{1}H-NMR. spectra were recorded on *Varian* A 60 and *Hitachi Perkin-Elmer* R 20-B instruments in CCl_4. Chemical shifts are given in ppm downfield from Me_4Si as an internal standard. Mass spectra were measured on an *Atlas* CH_4 spectrometer, inlet temp. 150°, electron energy 70 eV. The molecular ions (M^+) and the most intense fragment ions (*m/e*) of each group of fragments are given and their relative intensities are indicated in % of the base peak. IR. spectra of neat films were measured on a *Perkin-Elmer* 125 instrument and typical bands are reported in cm^{-1}. Gas chromatography (GC.) was performed using packed glass columns in *Carlo Erba* GT and *Varian* Aerograph 1800 instruments and metal capillary columns in a *Perkin-Elmer* 266 instrument.

Olefins A, 1–3. – *(*E*)- and (Z)-3-Methylpent-2-ene* ((*E*)- and (*Z*)-**1**) of > 98% purity were purchased from *Fluka*, Buchs.

*(*E*)- and (Z)-2,6-Dimethylundeca-1,6-diene* ((*E*)- and (*Z*)-**2** 60:40) were prepared (70%) by *Wolff-Kishner* reduction [14] of α-geranyl acetone (BASF, Ludwigshafen, mixture (*E*)/(*Z*) *ca.* 60:40). The mix-

ture was separated [purity > 98% (GC.)] by distillation using an efficient column (1 m) filled with glass helices.

(*E*)-**2**. B.p. 92°/5 Torr. – IR.: 3085, 1785, 1652, 885. – ^{1}H-NMR.: 0.90 (*t*, J = 6, H_3C–C(10)); 1.60 and 1.68 (2*s*, H_3C–C(2) and H_3C–C(6)); 4.64 (*m*, H_2C=C(2)); 5.10 (br. *t*, J = 6, HC(7)). – MS.: 180 (M^+, 3), 165 (2), 137 (6), 124 (45), 109 (32), 95 (55), 81 (90), 58 (100), 55 (66), 41 (60).

(*Z*)-**2**. B.p. 91°/5 Torr. – IR.: 3080, 1780, 1650, 895. – ^{1}H-NMR.: 0.90 (*t*, J = 6, H_3C–C(10)); 1.63 and 1.65 (2br. *s*, H_3C–C(2) and H_3C–C(6)); 4.65 (*m*, CH_2=C(2)); 5.08 (*t*, J = 6.5, HC(7)). – MS.: identical with that of (*E*)-**2**.

(E)- and (Z)-2,6,9-Trimethyldeca-1,6-diene ((*E*)- and (*Z*)-**3**) were prepared (65%) by *Wolff-Kishner* reduction [14] of a mixture of (*E*)- and (*Z*)-2,5,9-Trimethyldeca-4,9-dienal (*ca.* 65:35) [15] and were separated by distillation as above.

(*E*)-**3**. B.p. 89°/5 Torr. – IR.: 3085, 1785, 1640, 882. – ^{1}H-NMR.: 0.87 (*d*, J = 7, $(H_3C)_2$–C(9)); 1.56 and 1.70 (2*m*, H_3C–C(2) and H_3C–C(6)); 4.61 (*m*, H_2C=C(2)); 5.10 (*t*, J = 7, HC(7)). – MS.: 180 (M^+, 2), 165 (1), 137 (6), 124 (38), 109 (46), 95 (37), 81 (100), 69 (80), 68 (64), 55 (65), 41 (60).

(*Z*)-**3**. B.p. 88°/5 Torr. – IR.: 3080, 1780, 1650, 890. – ^{1}H-NMR.: 0.89 (2*d*, J = 6.5, $(CH_3)_2$–C(9)); 1.69 (*d*, H_3C–C(2) and H_3C–C(6)); 4.64 (*m*, H_2C=C(2)); 5.10 (*t*, J = 6, HC(7)). – MS.: identical with that of (*E*)-**3**.

Dye-sensitized photooxygenations were carried out in a standard *Pyrex* apparatus with a water-cooled mantle [16] and a volume of *ca.* 120 ml. O_2 (> 99%) was drawn from a calibrated storage burette by means of a membrane pump, and circulated through solutions of 0.05 mol of olefin **A** in 90 ml of ethanol/2-propanol 1:1 *(v/v)* containing 100 mg of rose bengal and 750 mg of anhydrous sodium acetate. The light source was a 125 Watt high pressure Hg lamp (*Philips* HPK) with an age of 100–300 h. The solutions were maintained at 18–20° and the O_2 consumption was recorded automatically [16]. Gas volumes were reduced to 0° and 760 Torr. In all cases, the absorption rate reached its maximum value (V_{max}) after *ca.* 10% conversion and then dropped continuously to *ca.* 0.5 ml/min when *ca.* 1 mol-equiv. had been absorbed. The oxygenations were normally stopped at 90–98% conversion to avoid overoxidation.

β-Values (M) were estimated according to [10], with 2,5-dimethylfuran as the reference compound, reacting with V_{max} = 62 ml O_2/min under identical conditions and usually reacts in rose bengal-sensitized photooxygenation with a quantum yield of *ca.* 0.8 mol/E [17].

The hydroperoxides **B**, **C**, and **D** were reduced by adding their solutions dropwise to a cooled (0°) solution of 1.0 g of $NaBH_4$ in 50 ml of ethanol and then stirring at RT. until the peroxide test (KI, aqueous acetic acid) was negative. Reduction with triphenylphosphine [18] or dimethyl sulfide gave the same results. The resulting mixtures of the alcohols **E**, **F**, and **G** were isolated by dilution with water, extraction with ether, washing with water, drying (Na_2SO_4), concentration, and bulb distillation.

Product distributions were determined by analysis of both the crude and the distilled alcohol mixtures, as follows. The distributions of the alcohols **4**, **5** and **6**, were determined by GC. from indexes (isothermal chromatograms) calculated by multiplying the peak heights by the retention times. Response factors were neglected. The distributions of the alcohols (*E*)-**7**, **8**, and (*E*)-**9**, and (*E*)-**10**, **11**, and (*E*)-**12**, respectively, were determined by combination of GC. and NMR. since (*E*)-**7** and **8**, and (*E*)-**10** and **11** could not be separated by GC. The proportions [(*E*)-**7** + **8**]:[(*E*)-**9**] and [(*E*)-**10** + **11**]:[(*E*)-**12**] were determined by GC. as above. The proportions (*E*)-**7**:**8** and (*E*)-**10**:**11** were determined by NMR. using both the crude mixtures and samples of the mixtures [(*E*)-**7** + **8**] and [(*E*)-**10** + **11**] isolated by preparative GC. All experiments were carried out several times and the product distributions were reproductible with a relative error of 10% both for the analyses by GC. alone and for those using GC. and NMR. The GC. detection limit for the absence of **4** and the NMR. detection limit (absolute errors) for the absence of (*E*)-**7** and (*E*)-**10** are both estimated to be 5%.

Individual experiments. – *Oxygenation of (*E*)-***1*** (V_{max} = 39 ml O_2/min; β = *ca.* 0.05) gave a mixture of 38% of 3-ethylbut-3-en-2-ol (**5**), 48% of 3-methylpent-1-en-3-ol (**6**), 7% of unreacted (*E*)-**1** (82% combined yield) and of 7% of unknowns, b.p. 20–55°/12 Torr. (*E*)- and (*Z*)-3-Methylpent-3-en-2-ol ((*E*)- and (*Z*)-**4**) were not detectable.

*Oxygenation of (Z)-***1** (V_{max} = 34 ml O_2/min; β = *ca.* 0.06) gave a mixture of 11% of (*E*)-**4**, 13% of **5**, 64% of **6**, 4% of unreacted (*Z*)-**1** (78% combined yield) and of 8% of unknowns, b.p. 20–55°/12 Torr. We suspect that some (*Z*)-**4** was also formed but were unable to separate it from (*E*)-**4**.

*Oxygenation of (*E*)-***2*** (V_{max} = 25 ml O_2/min; β = *ca.* 0.10) gave a mixture of 44% of 10-Methyl-6-

methylidene-undec-10-en-5-ol (**8**), 46% of (*E*)-2,6-dimethylundeca-1,7-dien-6-ol ((*E*)-**9**), 2% of unreacted (*E*)-**2** (77% combined yield) and of 8% of unknowns, b.p. 30–100°/5 Torr. The 6,10-dimethyl-undeca-6,10-dien-5-ols ((*E*)- and (*Z*)-**7**) were not detectable.

Oxygenation of (*Z*)-**2** (V_{max} = 22 ml O_2/min; β = *ca.* 0.13) gave a mixture of 16% of (*E*)-**7**, 9% of **8**, 63% of (*E*)-**9**, 4% of unreacted (*Z*)-**2** (75% combined yield) and of 8% of unknowns, b.p. 30–100°/5 Torr.

Oxygenation of (*E*)-**3** (V_{max} = 28 ml O_2/min; β = *ca.* 0.08) gave a mixture of 36% of 2,9-dimethyl-5-methylidene-dec-9-en-4-ol (**11**), 48% of (*E*)-2,5,9-trimethyldeca-3,9-dien-5-ol ((*E*)-**12**), 7% of unreacted (*E*)-**3** (80% combined yield) and of 9% of unknowns, b.p. 30–100°/5 Torr. (*E*)- and (*Z*)-2,5,9-Trimethyldeca-5,9-dien-4-ol ((*E*)- and (*Z*)-**10**) were not detectable.

Oxygenation of (*Z*)-**3** (V_{max} = 24 ml O_2/min; β = *ca.* 0.11) gave a mixture of 12% of (*E*)-**10**, 9% of **11**, 66% of (*E*)-**12**, 5% of unreacted (*Z*)-**3** (75% combined yield) and of 8% of unknowns, b.p. 40–100°/5 Torr.

Identification and spectra of alcohols 4–12. – Alcohols (*E*)-**7** and (*E*)-**10** were obtained as inseparable mixtures (GC.) with **8** and **11**, respectively (see above). All other alcohols were purified by preparative GC., on polar (Carbowax 20 M) and apolar (Silicone SE 30) columns, to > 98% purity and were identified from their spectra. (*E*)-**4** [19], and **6** [20] were also identified by comparison (spectra) with authentic samples.

(*E*)-**4**: IR.: 3350, 1670, 825. – ^{1}H-NMR.: 1.17 (*d*, *J* = 6, $H_3C(1)$), 1.61 (*d*, *J* = 7, $H_3C(5)$); 1.60 (*s*, $H_3C-C(3)$); 4.08 (*qa*, *J* = 6, HC(2)); 5.36 (*m*, HC(4)). – MS.: 100 (M^+, 26), 85 (100), 67 (33), 57 (27), 43 (92), 41 (55).

5: IR.: 3350, 3085, 1650, 895. – ^{1}H-NMR.: 1.07 (*t*, *J* = 7, $H_3C-CH_2-C(3)$); 1.20 (*d*, *J* = 6, $H_3C(1)$); 2.08 (*qa*, *J* = 7, $H_2C-C(3)$); 4.18 (*qa*, *J* = 6, HC(2)); 4.70 and 4.95 (2*m*, $H_2C(4)$). – MS.: 100 (M^+, 1), 85 (23), 71 (100), 57 (15), 43 (77), 41 (45).

6: IR.: 3400, 3080, 1645, 995, 915. – ^{1}H-NMR.: 0.85 (*t*, *J* = 6, $H_3C(5)$); 1.20 (*s*, $H_3C-C(3)$); 1.45 (*qa*, *J* = 6, $H_2C(4)$); 4.93 (*d* × *d*, *J* = 8 and 2, HC(1)); 5.15 (*d* × *d*, *J* = 11 and 2, HC(1)); 5.85 (*qa*, *J* = 11, HC(2)). – MS.: 100 (M^+, 1), 85 (20), 71 (100), 55 (20), 43 (72).

(*E*)-**7** (2:1 mixture with **8**). – Partial ^{1}H-NMR.: 1.60 (*s*, $H_3C-C(6)$); 3.87 (*t*, *J* = 7, HC(5)); 5.29 (*t*, *J* = 7, HC(7)).

8: IR.: 3350, 3080, 1790, 1645, 895 and 1005. – ^{1}H-NMR.: 0.94 (*t*, *J* = 6, $H_3C(1)$); 1.72 (*s*, $H_3C-C(10)$); 3.98 (*t*, *J* = 7, HC(5)); 4.68 (*m*, $H_2C(11)$); 4.81 and 4.96 (2*m*, $H_2C=C(6)$). – MS.: 196 (M^+, 1), 178 (4), 163 (2), 139 (27), 121 (43), 107 (27), 95 (80), 81 (65), 69 (82), 55 (80), 42 (100).

(*E*)-**9**: IR.: 3370, 3060, 1770, 1640, 985, 975. – ^{1}H-NMR.: 0.90 (*t*, *J* = 7, $H_3C(11)$); 1.20 (*s*, $H_3C-C(6)$); 1.70 (*s*, $H_3C-C(2)$); 4.62 (*m*, $H_2C(1)$); 5.48 (*m*, HC(7) and HC(8)). – MS.: 196 (M^+, < 1), 178 (1), 135 (3), 113 (100), 95 (10), 81 (15), 71 (92), 55 (18), 43 (33).

(*E*)-**10** (3:2 mixture with **11**). – Partial ^{1}H-NMR.: 1.59 (*s*, $H_3C-C(5)$); 3.92 (*d*, *J* = 7, HC(4)); 5.29 (*t*, *J* = 6, HC(6)).

11: IR.: 3360, 3085, 3080, 1650, 1642, 905, 895. – ^{1}H-NMR.: 0.92 (*d*, *J* = 7, $(H_3C)_2-C(2)$); 1.72 (*s*, $H_3C-C(9)$); 4.02 (*t*, *J* = 6, HC(4)); 4.63 (*m*, $H_2C(10)$); 4.78 and 4.98 (2*m*, $H_2C=C(5)$). – MS.: 196 (M^+, < 1), 178 (3), 135 (31), 121 (36), 95 (80), 81 (53), 69 (75), 55 (70), 43 (100), 41 (92).

(*E*)-**12**: IR.: 3370, 3080, 1780, 1645, 895, 980. – ^{1}H-NMR.: 1.00 (*d*, $(H_3C)_2-C(9)$); 1.19 (*s*, $H_3C-C(6)$); 1.68 (*s*, $H_3C-C(2)$); 4.62 (*s*, $H_2C(1)$); 5.44 (*m*, HC(7) and HC(8)). – MS.: 196 (M^+, < 1), 178 (1), 163 (1), 135 (4), 123 (4), 113 (100), 95 (25), 69 (18), 35 (15), 43 (82).

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265. Structural Studies of 1,8-Disubstituted Naphthalenes as Probes for Nucleophile-Electrophile Interactions[1])

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Summary

Results of crystal structure analyses of seven 1,8-disubstituted naphthalenes (**2a**, 8-(*N,N*-dimethylamino)-1-naphthyl methyl ketone; **2b**, 8-(*N,N*-dimethylamino)naphthalene-1-carboxylic acid; **2c**, methyl 8-(*N,N*-dimethylamino)naphthalene-1-carboxylate; **2d**, 8-methoxy-1-naphthyl methyl ketone; **2e**, 8-methoxynaphthalene-1-carboxylic acid; **2f**, *N,N*-dimethyl-8-methoxynaphthalene 1-carboxamide; **2g**, *N,N*-dimethyl-8-hydroxynaphthalene-1-carboxamide) with a nucleophilic centre ($N(CH_3)_2$, OCH_3, OH) at one of the *peri* positions and an electrophilic centre (carbonyl C) at the other are described. All seven molecules show a characteristic distortion pattern: the exocyclic bond to the electrophilic centre is splayed outward, and the one to the nucleophilic centre is splayed inward; the carbonyl C is displaced from the plane of its three bonded atoms towards the nucleophile. This distortion pattern differs from that found in other 1,8-disubstituted naphthalenes and is interpreted as an expression of incipient nucleophilic addition to a carbonyl group. The crystal structure of **2b** contains an ordered arrangement of equal numbers of amino acid and zwitterionic molecules.

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