217. Iron Carbonyl Induced Reactions of Norbornene Derivatives with Substituted Acetylenes

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(1.VIII.77)

Summary

Photochemical reactions of norbornadiene with substituted acetylenes in the presence of $Fe(CO)_5$ gave various products of different types, depending on the nature of the acetylene. The results are summarized in *Table 1.* The cyclopentanone **1** was always formed in these reactions. In the reaction of disubstituted acetylenes such as dimethyl acetylenedicarboxylate and ethyl phenylpropiolate, the cyclopentenones **2** and **5** were formed, respectively. By contrast, propiolic esters produced the cyclohexenones **3** and **4**, in which the ester group was attached on the β carbon with respect to the keto group. Plausible mechanisms for the formation of these products are shown in *Schemes 7* and *8.* The reaction of diphenylacetylene gave the cyclohexendione **7** as well as the cyclopentenone **6**. Two enedione products **8** and **9** were obtained from the reaction of phenylacetylene. Compound **9** was converted to the aromatic diacetate **13** by heating with acetic anhydride in pyridine. On irradiation in the presence of $Fe(CO)_5$ norbornene reacted similarly with dimethyl acetylenedicarboxylate and phenylacetylene to give the cyclopentenone **14** and the cyclohexenone **15**, respectively. Compound **15**, upon heating, isomerized to hydroquinone **16**, which on acetylation gave the diacetate **17**.

1. Introduction. - Norbornadiene is known to behave like acetylenes in some reactions with metal carbonyls [1], and indeed five ketonic and four dimeric products have been isolated from the reaction with iron pentacarbonyl [2]. Among the products cyclopentanone **1** was fully characterized and assigned as the *exo-trans-exo* configuration [3] [4]. The analogous iron carbonyl induced reactions of various norbornene derivatives were extensively studied [5-7] and formation of cyclopentanones of type **1** was shown to be the general and stereospecific reaction [8]. However, such coupling reaction between different kind of molecules was scarcely studied, in spite of its potential synthetic utility.

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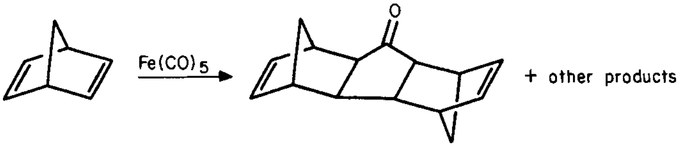
[1]) Deceased December 19, 1976.

Scheme 1



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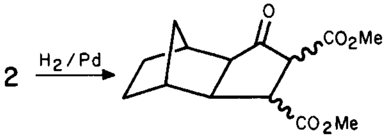
Therefore, we have investigated iron carbonyl induced reactions of norbornadiene and norbornene with some acetylene derivatives[2]).

2. Results. - 2.1. *Reactions of norbornadiene.* Among several known procedures for the reactions of iron carbonyls with organic ligands [10], the photochemical reaction using iron pentacarbonyl ($Fe(CO)_5$) was investigated[3]). The ethereal solutions containing acetylenic compounds, 1.0-1.5 mol-equiv. of $Fe(CO)_5$, and a large excess of norbornadiene were irradiated with a 150 W mercury high-pressure lamp through a pyrex filter for 3-4 h. The results are summarized in *Table 1.* In these reactions the excess of norbornadiene was needed to obtain the cross coupling compounds. Nevertheless, cyclopentanone **1** was always formed under these conditions[4]).

The cyclopentanone structure of **2** was deduced from its IR. (1745, 1725, and 1700 cm^{-1}), mass (M^+ 262), and UV. spectra. In the ^{1}H-NMR. spectrum, no appropriate couplings both between H−C(3a) and H−C(4), and between H−C(7a) and H−C(7) indicated the *exo*-configuration (*cf.* [3]). Catalytic hydrogenation of **2** gave the perhydro-compound **10** which was shown to be in equilibrium with the enol-forms by the IR. and ^{1}H-NMR. spectra (*cf.* exper. part).

Scheme 2



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The cyclohexenone structure of **3** and **4** [11] was indicated by their IR. (**3**, 1720 and 1670 cm^{-1}; **4**, 1720 and 1675 cm^{-1}) and UV. spectra. The ^{1}H-NMR. spectra of **3** and **4** showed only one olefinic proton signal (H−C(6)) at δ 6.58 with no apparent

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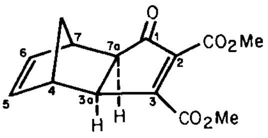
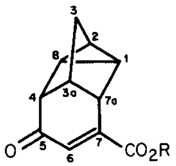
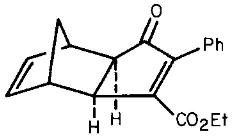
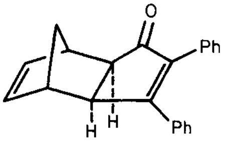
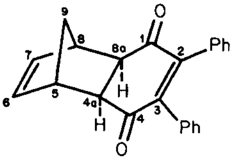
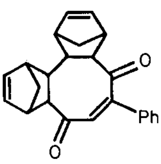
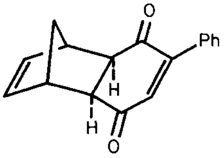
[2]) Reactions with olefinic compounds will be reported later [9].

[3]) In some cases, thermal reaction using $Fe_2(CO)_9$ was also investigated, but the results were less satisfying.

[4]) As yet no attempt has been made to optimize the conversion. However, when the reaction was carried out using equimolar amounts of substrates or excess of the acetylene, no product formation was observed.

Table 1. *Products from iron pentacarbonyl induced reactions of norbornadiene with acetylenes*

Acetylenes	Products	(Yield in %)[a])
CO_2Me C III C CO_2Me b)	 **2** (24)	**1** (18)
H C III C CO_2R	 **3**, R=Me (13) **4**, R=Et (2)	**1** (15) (10)
Ph C III C CO_2Et b)	 **5** (8)	**1** (33)
Ph C III C Ph b)	 **6** (20)  **7** (7)	**1** (38)
H C III C Ph	 **8** (7)  **9** (10)	**1** (24)

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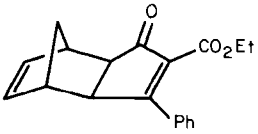
[a]) Yields are based on $Fe(CO)_5$ used.

[b]) The reaction mixture was treated with ceric ammonium nitrate, prior to the product isolation.

vicinal coupling, suggesting that the β carbon (C(7)) with respect to the carbonyl group was substituted with the ester group.

The structural similarlity of **5** and **2** was evident from a comparison of their NMR. spectra, one ester group being replaced by a phenyl group in **5**. Although the regioisomer **11** cannot be ruled out by these data, **5** is considered to be a more preferable structure by the following experiment. Catalytic hydrogenation of the product gave a mixture of the perhydro-derivatives. The ^{1}H-NMR. and IR. ($\tilde{\nu}$(CO) 1728 (br.) cm^{-1}) spectra of the mixture showed no evidence for the enol compound, suggesting that the ester group is bonded to C(3), since the presence of a ester group at C(2) (*i.e.*, the β-ketoester) in **10** caused predominantly the enol form.



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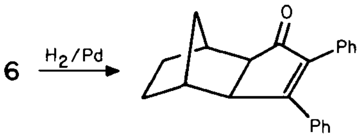
The structure of **6** was similarly determined by the IR., mass and ^{1}H-NMR. spectra, being identical with that reported by *Pauson et al.* [12]. In contrast to **2** and **5**, catalytic hydrogenation of **6** under the same reaction conditions yielded only the dihydro-derivative **12** [12].

Scheme 3



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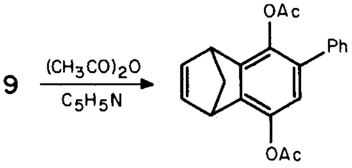
Enedione structure of **7** was deduced from its elemental analysis, mass (M^+ 326) and characteristic UV. spectra (*cf.* exper. part). In the ^{1}H-NMR. spectrum, a pairwise equivalence of the vinylic (δ 6.35), allylic methine (δ 3.39), and methine protons (δ 2.73) *a* to the carbonyl group reflected the presence of a plane of symmetry within the molecule. The *exo*-configuration at C(4a) (or C(8a)) was suggested by the absence of appropriate coupling between H–C(5) (resp. H–C(8)) and H–C(4a) (resp. H–C(8a)).

The structure of **9** [13] was similarly determined on the basis of the spectroscopic data. Furthermore, compound **9** was converted to the diacetate **13** (45%) by heating with acetic anhydride in pyridine.

Compound **8** was shown by the elemental analysis and mass spectrum (M^+ 342) to contain two norbornadiene molecules, two carbonyl groups and one phenylacetylene moiety. The enedione structure was reasonably suggested by its IR. and UV. spectra, the latter being very similar in the absorption pattern to that of **9**. In the ^{1}H-NMR. spectrum, one olefinic proton appeared at δ 6.43 as a singlet and four

Scheme 4



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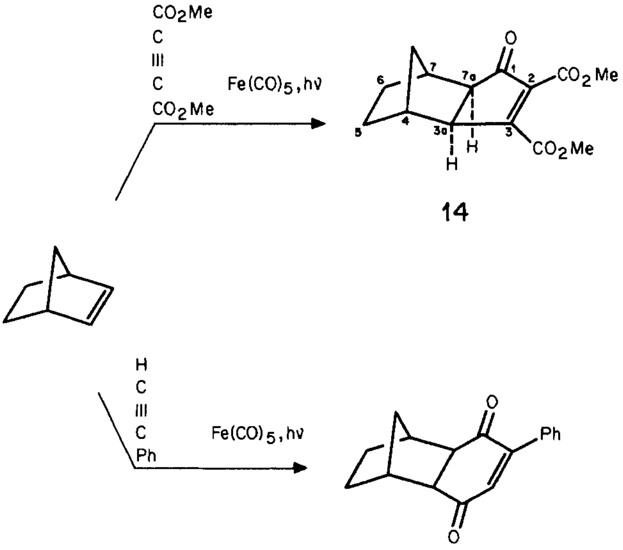
protons at δ 6.33-5.95 as multiplet. Of aliphatic protons six protons were revealed at relatively low field (δ 2.96-2.62), these being allylic and in α-position to the carbonyl group. The configuration at the ring junctions still remains unclear.

2.2. *Reactions of norbornene.* Norbornene reacted similarly with some acetylenes, though the yields were low. Irradiation of dimethyl acetylenedicarboxylate and $Fe(CO)_5$ in the presence of a large excess of norbornene yielded the cyclopentenone **14** in 9% yield *(Scheme 5).*

The exo configuration at C(3a) (resp. C(7a)) was deduced from the absence of proton coupling between H–C(3a) (resp. H–C(7a)) and H–C(4) (resp. (H–C(7)).

The analogous reaction of phenylacetylene gave the adduct **15** in 5% yield *(Scheme 5).* The structure was determined by IR., UV., mass, and ^{1}H-NMR. spectra. Compound **15**, on heating at 120-150°, isomerized to the hydroquinone **16** (IR. 3350 cm^{-1}), its acetylation giving the diacetate **17** (IR. 1765 cm^{-1}) in 86% yield. In contrast, methyl propiolate was not reactive under the coupling reaction conditions.

Scheme 5



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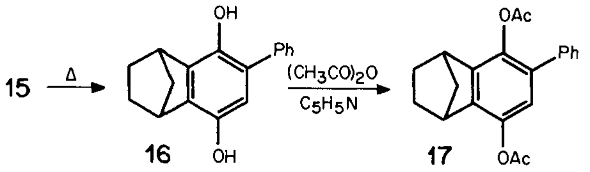
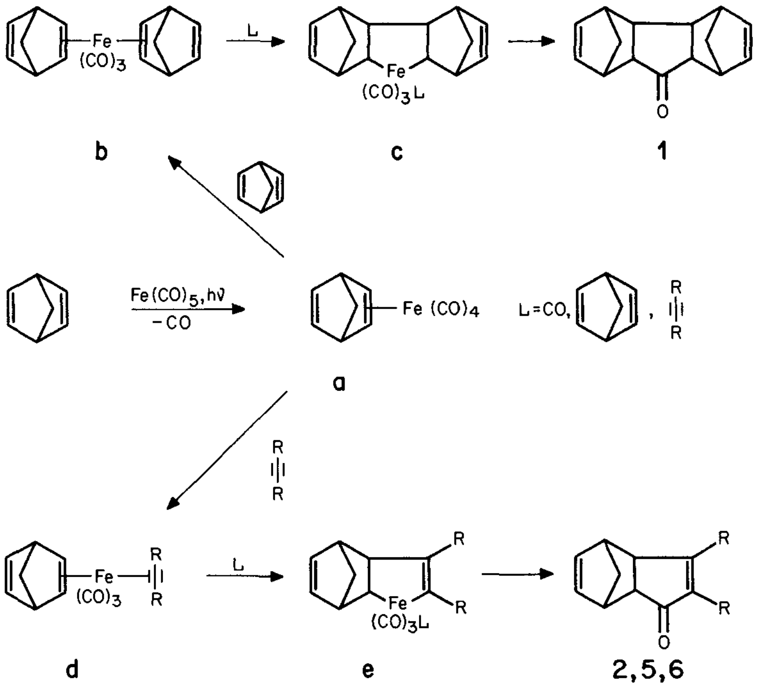
Scheme 6



3. Discussion. - Depending on the nature of the acetylene, various products of different types were obtained. Reactions of the disubstituted acetylenes gave the cyclopentenones **2**, **5**, **6**, and **14** as main product besides the cyclopentanone **1**. The formation of these products can be explained in the similar way to that discussed for the cyclopentanone formation from norbornene derivatives [5] [8] *(Scheme 7).*

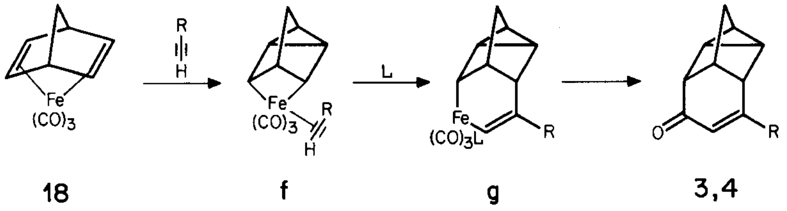
Scheme 7



Since a large excess of norbornadiene was used[4]), the reaction might be initiated by complexation of the iron tetracarbonyl with norbornadiene to give **a**. Further replacement of a CO ligand of **a** with norbornadiene or an acetylene molecule gives **b** or **d**, their oxidative coupling followed by migratory insertion yielding the cyclopentanone **1** and the cyclopentenones **2**, **5**, and **6**, respectively. *Pauson et al.* [12] have reported the similar cyclopentenone formation by the reaction of the strained olefin with acetylenehexacarbonyldicobalt complexes, although the reaction was limited to acetylenes with electron-donating groups.

In contrast, the reaction of propiolic esters gave the cyclohexenones **3** and **4** instead of the cyclopentenone. These products are probably derived from the initial formation of the norbornadiene-iron tricarbonyl complex **18** [14] [15] followed by the oxidative coupling and migratory insertion as shown in *Scheme 8*.

Scheme 8



In the reactions of phenylacetylene and diphenylacetylene, the products incorporating two carbonyl groups were obtained. The similar quinone derivative formation has been observed in the reactions of iron carbonyls with substituted acetylenes [10] [16].

It should be noted that the iron carbonyl induced reaction between norbornene derivatives and acetylenes occurred concurrently with carbonyl insertion to give the cyclic ketones, while the analogous reaction of norbornadiene with olefinic compounds gave acyclic coupling products^2).

The support of this work by the *Swiss National Foundation of Science* is gratefully acknowledged. We are grateful to Professor *H.-J. Hansen*, University of Fribourg, for his useful discussion and encouragement. We thank the Analytical Department of the Institute.

Experimental Part

General. - M.p. were taken on a *Mettler* FP-2 apparatus. Mass spectra (MS.) were taken on a *CEC*-21-110B mass spectrometer at an ionizing voltage of 70 eV and data are expressed in *m/e* (rel. %). Infrared (IR.) data are given in units of wave numbers (cm^{-1}). UV. spectra were measured in methanol and data (sh = shoulder) are expressed in nm (ε). The proton magnetic resonance (^{1}H-NMR.) spectra were measured, unless otherwise stated, on a 60 MHz spectrometer in CDCl$_3$. The chemical shifts are expressed as δ values (ppm) with tetramethylsilane as an internal standard ($\delta = 0$); *s* = singlet, *d* = doublet, *t* = triplet, *qa* = quartet, *m* = multiplet, br. = broad. The coupling constants are given in Hz.

Analytical gas-liquid phase chromatography (GLC.) was performed on *C. Erba* apparatus, using a glass capillary column coated with XE-60 [17]. Analytical and preparative thin layer chromatography (TLC. and prep. TLC.) were carried out on Polygram silica gel and on silica gel 60F$_{254}$ (*Merck*, Fertigplatten), respectively. For column chromatography silica gel 60 (*Merck*) was used. Distillations were done in a bulb tube (Kugelrohr), using *Büchi* GKR-50 distillation apparatus. Abbreviations: RT. = room temperature, i.V. = *in vacuo*.

1. General procedure for photochemical reactions of olefins and acetylenes in the presence of iron pentacarbonyl (Fe(CO)$_5$). - The ethereal solution containing acetylenic compound, 1.0-1.5 mol-equiv. of Fe(CO)$_5$, and a large excess of norbornadiene or norbornene in a half-cylindric quartz vessel [18] was flushed with nitrogen prior to photolysis, which was carried out under nitrogen with cooling by water using a 150 W mercury high-pressure lamp (TQ-150, *Quarzlampengesellschaft* m.b.H. Hanau) equipped with a Pyrex filter. Under these conditions no dark reaction was observed. The photochemical reaction was monitored by TLC.

2. Photochemical reaction of norbornadiene and dimethyl acetylenedicarboxylate in the presence of $Fe(CO)_5$. - A solution of 2.0 g (21.7 mmol) of norbornadiene, 300 mg (2.1 mmol) of dimethyl acetylenedicarboxylate, and 550 mg (2.8 mmol) of $Fe(CO)_5$ in 100 ml of ether was irradiated for 3 h. During this time the solution became heterogeneous. The mixture was filtered and the solvent evaporated under reduced pressure. The black residue was redissolved in 10 ml of methanol and 1.2 g (2.2 mmol) of ceric ammonium nitrate added. The mixture was stirred at RT. for 30 min. After the solvent was evaporated, water was added and the products repeatedly extracted with methylene chloride. The combined organic layers were dried (Na_2SO_4), filtered, and evaporated. Chromatography of the residue on a silica gel column with chloroform gave, in order of elution, 30 mg (10%) of unreacted dimethyl acetylenedicarboxylate, 131 mg (22%)[5] of **1**, m.p. 83-84° (ethanol), lit., m.p. 85° [1], and 133 mg (24%) of exo-*2,3-bismethoxycarbonyl-4,7-methano-3a,4,7,7a-tetrahydroinden-1-one* (**2**). Colourless prisms, m.p. 82-83° (ether). - UV.: $\lambda_{max}=209$ (6220, sh), 228 (7200). - IR. (KBr): 1745 (CO_2CH_3), 1725 (CO_2CH_3), 1700 (CO), 1635, 1440, 1435, 1280, 1170, 1023, 1015. - ^{1}H-NMR. (100 MHz): 6.38-6.14 (8-line *m*, H-C(5) and H-C(6)); 3.05 (*d*, superimposed by small *m*, $J=5.5$, H-C(7a) or H-C(3a)); 2.50 ($d \times d$, $J=5.5$, $J=1.0$, H-C(3a) or H-C(7a)); 1.50 and 1.33 (broadened *AB*-system, $J_{A,B}=10.0$, 2 H-C(8)). - MS.: 262 (M^+, 11), 230 (22), 202 (17,5), 198 (21), 165 (30), 115 (21), 66 (100).

$C_{14}H_{14}O_5$ (262.5) Calc. C 64.11 H 5.38% Found C 64.22 H 5.57%

3. Photochemical reaction of norbornadiene and alkyl propiolates in the presence of $Fe(CO)_5$. - 3.1. *With methyl propiolate.* A solution of 2.0 g (21.7 mmol) of norbornadiene, 300 mg (3.6 mmol) of methyl propiolate, and 800 mg (4.1 mmol) of $Fe(CO)_5$ in 100 ml of ether was irradiated for 4 h. The mixture was filtered, evaporated, and chromatographed on a silica gel column with chloroform to give 135 mg (16%)[5] of **1** and 96 mg (13%) of *methyl 5-oxo-1,2,4-metheno-2,3,3a,4,5,7a-hexahydro-1*H*-indene-7-carboxylate* (**3**). Colourless prisms, m.p. 94-95° (ether). - UV.: $\lambda_{max}=211$ (3610, sh), 245 (6260). - IR. (KBr): 2955, 1720 (CO_2CH_3), 1670 (CO), 1615, 1435, 1235, 1182, 1075. - NMR. (100 MHz): 6.58 (*d*, $J=1.0$, H-C(6)); 3.79 (*s*, H_3COCO); 2.88, 2.59, and 2.28 (3 small *m*, H-C(3a), H-C(4), and H-C(7a)); 1.92-1.44 (*m*, 4 H); 1.33 ($t \times m$, $J=5.0$, H-C(1) or H-C(2) or H-C(8)). - MS.: 204 (M^+, 89), 177 (27), 176 (15), 145 (19), 144 (16), 117 (100), 116 (50), 115 (54), 91 (31), 66 (54).

$C_{12}H_{12}O_3$ (204.22) Calc. C 70.57 H 5.92% Found C 70.34 H 5.96%

3.2. *With ethyl propiolate.* A solution of 2.4 g (26.0 mmol) of norbornadiene, 600 mg (6.1 mmol) of ethyl propiolate, and 1.32 g (6.7 mmol) of $Fe(CO)_5$ in 200 ml of ether was irradiated for 3.5 h. After work-up, the residue was chromatographed on a silica gel column with chloroform to give 147 mg (10%)[5] of **1** and 25 mg (2%) of *ethyl 5-oxo-1,2,4-metheno-2,3,3a,4,5,7a-hexahydro-1*H*-indene-7-carboxylate* (**4**) [11], pale yellow oil, b.p. 90-93°/0.008 Torr. - UV.: $\lambda_{max}=219$ (4870, sh), 243 (6820). - IR. (film): 1720 (CO_2Et), 1675 (CO), 1623, 1235, 1188, 1075. - NMR. (100 MHz): 6.58 (br. *s*, H-C(6)); 4.27 (*qa*, $J=8.0$, CH_2CH_3); 2.93, 2.63, and 2.32 (3 small *m*, H-C(3a), H-C(4), and H-C(7a)); 1.94-1.14 (*m*, 5 H); 1.32 (*t*, $J=8.0$; CH_2CH_3). - MS.: 218 (M^+, 71), 190 (12), 173 (10), 161 (12), 145 (21), 144 (18), 117 (100), 116 (43), 115 (57), 91 (23), 66 (45).

$C_{13}H_{14}O_3$ (218.24) Calc. C 71.54 H 6.47% Found C 71.26 H 6.53%

4. Photochemical reaction of norbornadiene and ethyl phenylpropiolate in the presence of $Fe(CO)_5$. - A solution of 3.0 (32.6 mmol) of norbornadiene, 800 mg (4.6 mmol) of ethyl phenylpropiolate and 990 mg (5.1 mmol) of $Fe(CO)_5$ in 200 ml of ether was irradiated for 3 h. After evaporation of the solvent the mixture was treated with 5.0 g (9.1 mmol) of ceric ammonium nitrate in ethanol. Work-up followed by chromatography on a silica gel column with benzene gave 68 mg (8.5%) of ethyl phenylpropiolate, 353 mg (33%)[5] of **1** and 110 mg (8%) of exo-*2-phenyl-3-ethoxycarbonyl-4,7-methano-3a,4,7,7a-tetrahydroinden-1-one* (**5**). Pale yellow prisms, m.p. 55-56° (hexane). - UV.: $\lambda_{max}=223$ (5880), 281 (1920); $\lambda_{min}=257$ (1850). - IR. (KBr): 3060, 2970, 2935, 1710 (CO_2Et), 1700 (CO), 1445, 1370, 1322, 1265, 1258, 1232, 1163, 1138, 1012, 738, 710, 695. - NMR. (100 MHz): 7.43 (*s*, 5 aromat. H); 6.55-6.30 (*m*, H-C(5) and H-C(6)); 4.27 (*qa*, O-CH_2CH_3); 3.17 (*d*, $J=6.0$, superimposed by *m*, H-C(3a) or H-C(7a)); 3.18-3.03 (*m*, H-C(4) and H-C(7)); 2.59 ($d \times d$, $J=6.0$, $J=1.0$, H-C(7a) or H-C(3a)); 1.56 and 1.44 (broadened *AB*-system $J_{A,B}=10.0$, 2 H-C(8)); 1.16 (*t*, $J=7.0$, CH_2CH_3). - MS.: 294 (M^+, 69), 266 (19), 249 (19),

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[5] The yields are calculated on the basis of $Fe(CO)_5$ used.

248 (32), 228 (100), 221 (62), 220 (44), 200 (60), 172 (58), 156 (57), 155 (53), 128 (45), 127 (60), 115 (45), 77 (39), 56 (40).

$C_{19}H_{18}O_3$ (294.33) Calc. C 77.53 H 6.16% Found C 77.35 H 6.32%

5. Photochemical reaction of norbornadiene and diphenylacetylene in the presence of $Fe(CO)_5$. - A solution of 2.0 g (21.7 mmol) of norbornadiene, 600 mg (3.4 mmol) of diphenylacetylene, and 1.0 g (5.1 mmol) of $Fe(CO)_5$ in 200 ml of tetrahydrofuran was irradiated for 3.5 h. After removal of the solvent, the mixture was treated with 1.0 g (1.8 mmol) of ceric ammonium nitrate in 10 ml of methanol at RT. After work-up the residue was chromatographed on a silica gel column with benzene to give, in order of elution, 255 mg (42.5%) of diphenylacetylene, 408 mg (38%)[5]) of **1**, and 350 mg of a mixture of **6** and **7** Isolation of these products was performed by fractional recrystallization from ether to give 205 mg (20%) of **6** and 80 mg (7%) of **7**.

exo-*2,3-Diphenyl-4,7-methano-3a,4,7,7a-tetrahydroinden-1-one* (**6**). Colourless prisms, m.p. 119-120° (ether), lit., m.p. 117-118° [12]. - UV.: λ_{max}=211 (13510), 228 (16310), 301 (10750); λ_{min}=215 (12910), 267 (5960). - IR. (KBr): 3060, 2975, 1695 (CO), 1350, 1343, 1270, 796, 745, 695. - NMR.: 7.32-7.15 (m, 10 aromat. H); 6.28 (*t*, *J*=1.8, H–C(5) and H–C(6)); 3.30 (*d*, *J*=5.6, H–C(3a) or H–C(7a)); 3.10 (*m*, H–C(4) or H–C(7)); 2.65-2.51 (*m*, 2 H); 1.43 (small *m*, 2 H–C(8)). - MS.: 298 (M^+, 51), 270 (4), 232 (100), 231 (17), 204 (9.5), 203 (14), 202 (12), 178 (10), 102 (22).

$C_{22}H_{18}O$ (298.36) Calc. C 88.56 H 6.08% Found C 88.71 H 6.11%

2,3-Diphenyl-5,8-methano-1,4,4a,5,8,8a-hexahydronaphthalene-1,4-dione (**7**). Yellow needles, m.p. 150-152° (ether). - UV.: λ_{max}=213 (9780, sh), 229 (12470), 308 (4400); λ_{min}=265 (3260). - IR. (KBr): 1685 (CO), 1667 (CO), 1442, 1325, 692. - NMR.: 7.32-6.86 (*m*, 10 aromat. H); 6.35 (*t*, *J*=2.0, H–C(2) and H–C(3)); 3.39 (*m*, H–C(1) and H–C(4)); 2.73 (*s*, H–C(4a) and H–C(8a)); 1.45 (small *m*, 2 H–C)9)). - MS.: 326 (M^+, 38), 298 (40), 260 (43), 232 (100), 200 (18), 178 (30), 102 (30), 91 (11), 66 (33).

$C_{23}H_{18}O_2$ (326.37) Calc. C 84.64 H 5.56% Found C 84.48 H 5.63%

6. Photochemical reaction of norbornadiene and phenylacetylene in the presence of $Fe(CO)_5$. - A solution of 3.0 g (32.6 mmol) of norbornadiene, 600 mg (5.9 mmol) of phenylacetylene, and 1.2 g (6.1 mmol) of $Fe(CO)_5$ in 200 ml of ether was irradiated for 3 h. After work-up the residue was chromatographed on a silica gel column with benzene to give 147 mg (7%) of **8**, 317 mg (24%)[5]) of **1**, and 149 mg (10%) of **9**.

Compound **8**. Colourless prisms, m.p. 131-132° (ether). - UV.: λ_{max}= 206 (7695), 229 (5985), 293 (5640); λ_{min}=215 (5130), 258 (2565). - IR. (KBr): 1703 (CO), 1665 (CO), 1597, 1575, 1170, 748, 720, 712. - NMR.: 7.39 (br. *s*, 5 aromat. H); 6.43 (*s*, 1 H); 6.33-5.95 (*m*, 4 H); 2.96-2.62 (*m*, 6 H); 2.33-1.80 (*m*, 4 H); 1.53-1.26 (*m*, 2 H). - MS.: 342 (M^+, 6), 277 (58), 259 (11), 231 (10), 211 (28), 183 (25), 181 (15), 115 (17), 102 (18), 91 (23), 66 (100).

$C_{24}H_{22}O_2$ (342.42) Calc. C 84.17 H 6.47% Found C 83.86 H 6.35%

2-Phenyl-5,8-methano-1,4,4a,5,8,8a-hexahydronaphthalene-1,4-dione (**9**). Yellow viscous oil, b.p. 145-150°/0.01 Torr. - UV.: λ_{max}=207 (17690), 225 (22690), 299 (11540); λ_{min}=212 (16920), 256 (3850). - IR. ($CHCl_3$): 1673 (CO), 1605, 1448, 1165, 692. - NMR.: 7.41 (*s*, 5 aromat. H); 6.84 (*s*, H–C(7)); 6.30 (*t*, *J*=1.8, H–C(2) and H–C(3)); 3.33 (*m*, H–C(1) and H–C(4)); 2.62 (*AB*-system, $J_{A,B}$=9.0, H–C(4a) and H–C(8a)); 1.37 (small *m*, 2 H–C(9)). - MS.: 250 (M^+, 26), 185 (9), 128 (6), 102 (24), 91 (13), 66 (100).

$C_{17}H_{14}O_2$ (250.28) Calc. C 81.58 H 5.64% Found C 81.72 H 5.81%

7. Hydrogenation of 2. - A solution of 30 mg (0.11 mmol) of **2** in 25 ml of methanol was hydrogenated over 25 mg of 5% Pd/C at atmospheric pressure. The catalyst was filtered off, and the filtrate concentrated under reduced pressure to give 28 mg (92%) of the perhydroderivative **10**. Colourless prisms, m.p. 94-95.5° (ether). - UV.: λ_{max}=249 (5450). - IR. (KBr): 3250 (OH), 2960, 2950, 2918, 1738 (CO), 1665 (CO), 1625 (C=C), 1443, 1350, 1325, 1228, 1193, 1160, 1150, 1125, 795. - NMR.: 10.34 (br. *s*, 0.64 H); 4.01-3.65 (*m*, 0.36 H); 3.72 (*s*, superimposed by *m*, 2 × H_3C–O); 2.80-0.90 (*m*, 11 H). - MS.: 266 (M^+, 7), 234 (6), 208 (15), 207 (100), 176 (11), 175 (80), 107 (26), 91 (10), 79 (11), 72 (8), 67 (11).

$C_{14}H_{18}O_5$ (266.28) Calc. C 63.14 H 6.81% Found C 63.32 H 6.7%

8. Hydrogenation of 5. - A solution of 28 mg (0.09 mmol) of **5** in 10 ml of ethanol was hydrogenated over 35 mg of 10% Pd/C at RT. for 3 h. The catalyst was filtered off, the filtrate concentrated under reduced pressure, and the residue distilled at 130-140°/0.008 Torr to give 20 mg (70%) of colourless oil. - IR. ($CHCl_3$): 2950, 2870, 1728 (CO, br.), 1603, 1497, 1462, 1449, 1380, 1298, 1180, 1165, 1150, 697. - NMR.: 7.34-7.10 (*m*, 5 aromat. H); 4.04-3.20 (*m*, 3 H); 2.56-0.80 (*m*, 11 H); 0.95 (*t*, *J* = 7.0, superimposed by *m*, CH_2CH_3). - MS.: 298 (M^+, 31), 284 (24), 238 (17), 226 (19), 225 (92), 211 (26), 210 (61), 107 (25), 196 (100), 168 (27), 131 (41), 129 (31), 128 (32), 117 (30), 115 (34), 91 (59).

9. Hydrogenation of 6. - A solution of 16 mg (0.05 mmol) of **6** in 15 ml of ethanol was hydrogenated over 15 mg of 5% Pd/C. The work-up gave 15 mg (93%) of *2,3-diphenyl-4,7-methano-3a,4,5,6,7,7a-hexahydroinden-1-one* (**12**) [12]. Colourless prisms, m.p. 130-131° (hexane). - UV.: λ_{max} = 226, (3435), 295 (2600); λ_{min} = 254 (1380). - IR. (KBr): 2950, 2865, 1688 (CO), 1613, 1485, 1445, 1350, 1192, 1160, 730, 695. - NMR.: 7.28 (small *m*, 10 aromat. H); 3.16 (*d*, *J* = 6.0, H-C(3a) or H-C(7a)); 2.58 (small *m*, H-C(4) or H-C(7)); 2.46 (*d*, *J* = 6.0 superimposed by *m*, H-C(7a) or H-C(3a)); 2.10 (small *m*, H-C(7) or H-C(4)); 1.77-0.98 (*m*, 6 H). - MS.: 300 (M^+, 100), 234 (46), 232 (28), 215 (12), 204 (11), 203 (11), 178 (13), 165 (8), 128 (7), 115 (7.5), 102 (12), 91 (9), 77 (7.5).

$C_{22}H_{20}O$ (300.38) Calc. C 87.96 H 6.71% Found C 87.81 H 6.65%

10. Isomerization of compound 9. - A solution of 33 mg (0.13 mmol) of **9** and 350 mg (3.4 mmol) of acetic anhydride in 5 ml of pyridine was heated in a sealed tube at 100° for 6 h. The mixture was cooled to RT., reduced i.V., and redissolved in 20 ml of ether. The solution was washed with 1N HCl, 10% aqueous Na_2CO_3-solution, and water, and dried over Na_2SO_4. After evaporation of the solvent, the mixture was chromatographed on prep. TLC. with benzene to give 11 mg (33%) of unreacted **9** and 20 mg (45%) of *2-phenyl-5,8-methano-5,8-dihydronaphthalene-1,4-diyl diacetate* (**13**) as colourless viscous oil, b.p. 145-148°/0.008 Torr. - UV.: λ_{max} = 218 (30090), 256 (12680); λ_{min} = 240 (10860). - IR. ($CHCl_3$): 1762 ($OCOCH_3$), 1372, 1175. - NMR.: 7.33 (*s*, 5 aromat. H); 6.82 (*t*, *J* = 2.0, H-C(2) and H-C(3)); 6.67 (*s*, H-C(7)); 3.87 (*m*, H-C(1) and H-C(4)); 2.30 (*s*, H_3CCO); 2.15 (small *m*, 2 H-C(9)); 2.09 (*s*, H_3CCO). - MS.: 334 (M^+, 27), 292 (25), 250 (100), 78 (19), 43 (28).

$C_{21}H_{18}O_4$ (334.35) Calc. C 75.43 H 5.43% Found C 75.56 H 5.37%

11. Photochemical reaction of norbornene and dimethyl acetylenedicarboxylate in the presence of $Fe(CO)_5$. - A solution of 2.1 g (22.3 mmol) of norbornene, 300 mg (2.1 mmol) of dimethyl acetylenedicarboxylate, and 550 mg (2.8 mmol) of $Fe(CO)_5$ in 100 ml of ether was irradiated for 4 h. After evaporation of the solvent, the residue was chromatographed on a silica gel column with benzene/acetone 40:1 to give 51 mg (9%) of exo-*2,3-bismethoxycarbonyl-4,7-methano-3a,4,5,6,7,7a-hexahydroinden-1-one* (**14**), pale yellow oil, b.p. 130-135°/0.008 Torr. - UV.: λ_{max} = 212 (4920, sh), 240 (6220). - IR. (film): 2960, 1748 (CO_2CH_3), 1725 (CO_2CH_3), 1710 (CO), 1640, 1435, 1342, 1270, 1210, 1175, 1025, 680. - NMR. (100 MHz): 3.85 and 3.82 (2 *s*, 2 × H_3COCO); 2.94 (*d*, *J* = 5.5, H-C(3a) or H-C(7a)); 2.52 (br. *s*, H-C(4) and H-C(7)); 2.40 (*d*, *J* = 5.5, H-C(7a) or H-C(3a)); 1.89-0.98 (*m*, 6 H). - MS.: 264 (M^+, 80), 233 (59), 232 (55), 200 (100), 198 (49), 166 (88).

$C_{14}H_{16}O_5$ (264.27) Calc. C 63.62 H 6.10% Found C 63.80 H 6.23%

12. Photochemical reaction of norbornene and phenylacetylene in the presence of $Fe(CO)_5$. - A solution of 4.0 g (42.5 mmol) of norbornene, 600 mg (5.9 mmol) of phenylacetylene, and 1.2 g (6.1 mmol) of $Fe(CO)_5$ in 200 ml of ether was irradiated for 3 h. The mixture was filtered and the solvent removed i.V. Chromatography of the residue on a silica gel column with benzene gave 69 mg (5%) of *2-phenyl-5,8-methano-1,4,4a,5,8,8a-hexahydronaphthalene-1,4-dione* (**15**), yellow prisms, m.p. 96-95° (ether). - UV.: λ_{max} = 209 (6220), 225 (8740), 298 (5545); λ_{min} = 211 (6130), 258 (1680). - IR. (KBr): 1682 (CO), 1668 (CO), 1610, 1450, 695. - NMR.: 7.40 (*s*, 5 aromat. H); 6.84 (*s*, H-C(7)); 2.81 (br. *s*, H-C(1), H-C(4), H-C(4a), and H-C(8a)); 1.66-1.43 (*m*, 4 H); 1.37-1.20 (*m*, 2 H). - MS.: 252 (M^+, 63), 224 (15), 198 (28), 173 (26), 158 (23), 103 (13), 102 (100), 80 (22).

$C_{17}H_{16}O_2$ (252.30) Calc. C 80.92 H 6.39% Found C 81.15 H 6.28%

13. Thermal isomerization and acetylation of the compound 15. - In a bulb tube 57 mg (0.23 mmol) of **15** was placed and heated at 120-150° under ambient atmosphere. After 30 min the mixture was distilled at 140–150°/0.008 Torr to give 22 mg (39%) of *2-phenyl-5,8-methano-5,6,7,8-tetrahydronaphthalene-1,4-diol* (**16**) as viscous oil. - IR. (film): 3350 (br. OH), 2960, 2925, 2870, 1603, 1470, 1195, 1155, 1118, 1045, 872, 863, 795, 770. - NMR.: 7.37 (*s*, 5 aromat. H); 6.44 (*s*, 1 H); 4.74 (small *m*, 2×HO); 3.63–3.45 (*m*, 2 H); 2.03–1.12 (*m*, 6 H).

A solution of 14 mg (0.05 mmol) of **16** and 150 mg (1.5 mmol) of acetic anhydride in 1 ml of pyridine was heated at 50° for 20 h. The usual work-up gave 16 mg (86%) of *2-phenyl-5,8-methano-5,6,7,8-tetrahydronaphthalene-1,4-diyl diacetate* (**17**) as colourless needles, m.p. 114.5–116° (hexane). - UV.: $\lambda_{\max} = 217$ (11210), 245 (7400); $\lambda_{\min} = 230$ (5270). - IR. ($CHCl_3$): 1765 ($OCOCH_3$), 1372, 1180. - NMR.: 7.32 (*s*, 5 aromat. H); 6.79 (*s*, H–C(7)); 3.32 (*m*, H–C(1) and H–C(4)); 2.26 and 1.95 (2 *s*, 2×H_3CCO); 1.95–1.15 (*m*, 6 H). - MS.: 336 (M^+, 22), 294 (38), 252 (100), 224 (49), 43 (41).

$C_{21}H_{20}O_4$ (336.37) Calc. C 74.98 H 5.99% Found C 75.24 H 6.27%

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