

72. Thermal and Photochemical Reactions of 1,2-Annulated Barrelenes and Hydrobarrelenes in the Presence of Transition-Metal Carbonyls

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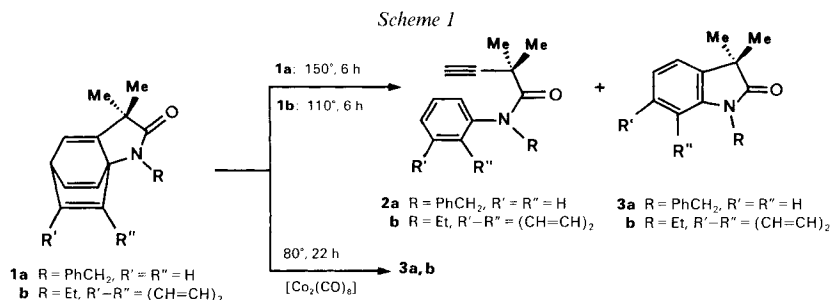
(28.II.89)

The $[\text{Co}_2(\text{CO})_8]$ -mediated *retro-Diels-Alder* reaction of the annulated barrelenes **1** afforded the 1*H*-indol-2(3*H*)-one derivatives **3** (Scheme 1), while the hydrobarrelene **4a**, under the same conditions, was converted to the anilide **6** (Scheme 2); **4b** remained unaffected. The direct irradiation of **1** led to the annulated cyclooctatetraenes **7** (Scheme 3). On irradiation in the presence of excess of $[\text{Fe}(\text{CO})_5]$, **1a**, **1b**, and **4a** gave the tricarbonyliron complexes **8**, **9**, and **11**, respectively (Schemes 3 and 4); under these conditions, **4b** was inert.

1. Introduction. – Recently, we reported on the synthesis of 1,2-five-ring-annulated barrelenes [1] and hydrobarrelenes [2] *via* the intramolecular *Diels-Alder* reaction of acylureas and acylamides, proceeding in some cases under surprisingly mild conditions [2]. In some cases, a tendency of the studied systems to undergo a *retro-Diels-Alder* reaction was observed [2] [3]. In this connection, we were interested to evaluate the thermal and photochemical stability of some of these tricyclic compounds and to elucidate the effect of metal-carbonyl complexation.

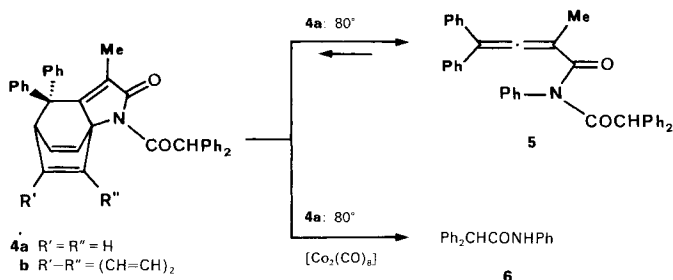
2. Thermal Reactions. – *1,2-Annulated Barrelenes.* The annulated barrelenes **1** were shown to give, on prolonged heating at 150° and at 110°, respectively, complex mixtures of products, among which were detected the *retro-Diels-Alder* compounds **2** and **3** (Scheme 1). However, at a lower temperature (80°), both **1a** and **1b** were found to be stable. Interestingly, in the presence of a slight excess of $[\text{Co}_2(\text{CO})_8]$ at 80°, **1** afforded as the only products in moderate yields the 1*H*-indol-2(3*H*)-ones **3** (Scheme 1). This shows unequivocally that only the *retro-Diels-Alder* reaction proceeding with loss of acetylene has been transition-metal-promoted. This is one of the few cases known in which this reaction becomes favourable in the presence of transition metals [4].

The structure of the 1*H*-indol-2(3*H*)-ones **3** was easily established on the basis of their spectral data (see *Exper. Part* and also [1]).



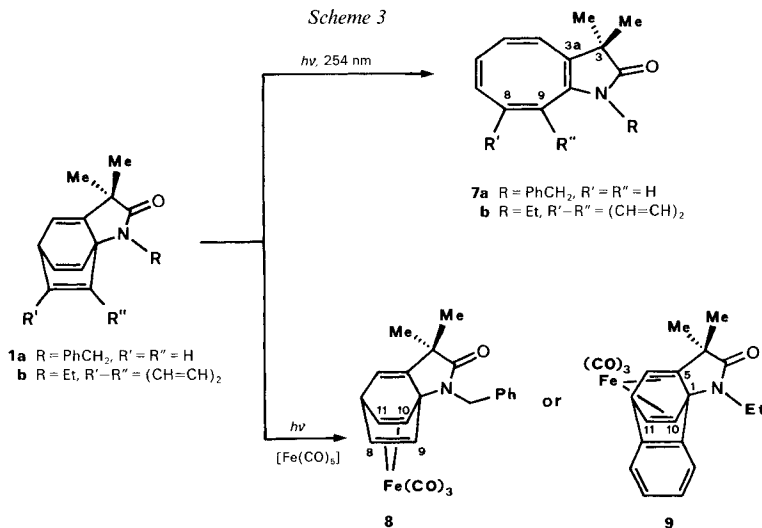
1,2-Annulated Hydrobarrelenes. The tricyclic compound **4a** gave, on heating at 80°, an equilibrium mixture of **4a** and the allenic acylamide **5** in a ratio of 4:1¹⁾ (Scheme 2). In the presence of $[\text{Co}_2(\text{CO})_8]$, however, at the same temperature, a complex mixture of products was obtained, the main component of which was shown to be the amide **6**. Under the same conditions, the benzo-annulated tricycle **4b** was shown to be stable in the absence and also in the presence of $[\text{Co}_2(\text{CO})_8]$.

Scheme 2



3. Photochemical Reactions. – 1,2-Annulated Barrelenes. On direct irradiation at 254 nm²⁾, the barrelenes **1** gave the yellow 1,2-five-ring-annulated cyclooctatetraenes **7** (Scheme 3). In contrast to the thermal reaction, this conversion was not affected by the presence of $[\text{Co}_2(\text{CO})_8]$.

Scheme 3



Characteristic for the structures of **7** were the large $^3J(\text{H}, \text{H})$ (ca. 11.5 Hz) through the $\text{C}=\text{C}$ bond and the small $^3J(\text{H}, \text{H})$ (ca. 3.5 Hz) values through the $\text{C}-\text{C}$ bond (see *Exper. Part* and [5]). Interestingly enough, one signal for

¹⁾ In this mixture, the allene **5** was evidenced by the allenic absorption in the IR spectrum at 1950 cm^{-1} and also by the characteristic absorption of the Me group at 2.06 ppm in the ^1H -NMR spectrum [2].

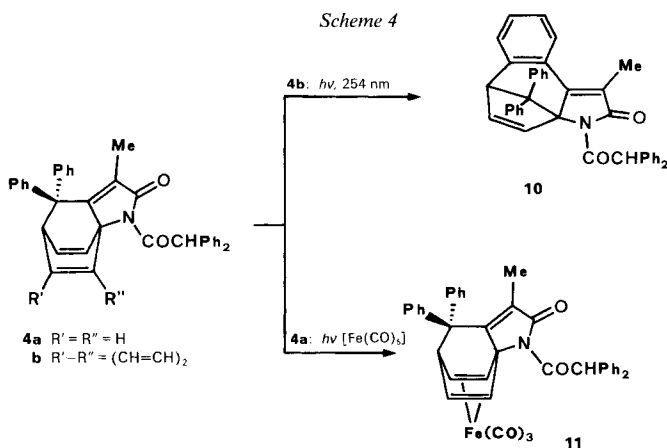
²⁾ Sensitization experiments with benzophenone, acetophenone, and acetone afforded intractable reaction mixtures.

both Me groups at C(3) was observed in the NMR spectra of **7a** ($^1\text{H-NMR}$: 1.23 ppm; $^{13}\text{C-NMR}$: 22.8 ppm), while the Me groups of **7b** gave two signals ($^1\text{H-NMR}$: 1.26 and 1.18 ppm; $^{13}\text{C-NMR}$: 23.3 and 21.8 ppm). In the $^1\text{H-NMR}$ spectrum of **7b**, two signals for the CH_2 protons (3.81 and 3.15 ppm) were observed. This diastereotopicity of the Me groups and of the CH_2 protons of **7b** must be attributed to the hindered ring inversion of the doubly annelated cyclooctatetraene ring [5] [6].

Irradiation of **1** in the presence of excess of $[\text{Fe}(\text{CO})_5]$ (*Solidex* filter) led to the formation of the iron complexes **8** and **9**³⁾ (*Scheme 3*). The structures of these complexes were easily established on the basis of the NMR spectral data.

Thus, the signal of $\text{H-C}(6)$ of **1a** in the $^1\text{H-NMR}$ spectrum remained practically unaffected by the complexation, while the signals of $\text{H-C}(8, 11)$ and $\text{H-C}(9, 10)$ of **8** were strongly shifted upfield ($\Delta\delta \approx 3.4$ ppm). Accordingly, the signals of C(8, 11) and of C(9, 10) in the $^{13}\text{C-NMR}$ spectrum were also very strongly shifted upfield ($\Delta\delta \approx 95$ ppm, see *Exper. Part*). The complexation of **9** was evidenced by the upfield-shift of the signals of $\text{H-C}(6)$, $\text{H-C}(10)$, and $\text{H-C}(11)$ ($\Delta\delta = 3.1$, *ca.* 3.5, and 3.35 ppm, resp.) and also of the signals of C(5), C(6), C(10), and C(11) ($\Delta\delta = 89.5$, *ca.* 90, 95, and 93 ppm, resp.).

1,2-Annelated Hydrobarrelenes. The hydrobarrelene **4a** gave, on direct irradiation at 254 nm, a complex photolysate. Under the same conditions, however, the benzo derivative **4b** gave a single photoproduct in good yield, having structure **10**⁴⁾ (*Scheme 4*). On irradiation in the presence of excess of $[\text{Fe}(\text{CO})_5]$ (*Solidex* filter), **4a** gave the iron complex **11** (*Scheme 4*). The benzo derivative **4b** gave no iron complex under the same conditions.



The complexation in **11** was substantiated by the NMR upfield-shifts of $\text{H-C}(8, 11)$ and $\text{H-C}(9, 10)$ ($\Delta\delta = 3.44$ and 3.21 ppm, resp.) and also of C(8, 11) and C(9, 10), engaged in the complexation ($\Delta\delta \approx 90$ ppm, see *Exper. Part*).

³⁾ In the case of **1a**, a second yellow unstable complex was detected by TLC but not isolated. On the basis of the IR spectrum and MS data, the composition $[\text{Fe}(\text{CO})_4 \cdot \text{L}]$ must be ascribed to this complex. It gave an unresolvable $^1\text{H-NMR}$ spectrum. In the case of **1b**, a trace amount ($< 1\%$) of another yellow complex was also detected but not isolated.

⁴⁾ The photochemical behaviour of **4a, b** is described in [7].

Experimental Part

1. *General.* See [2].

2. *Thermal Reactions of 1 in the Presence of $[Co_2(CO)_8]$.* A soln. of **1a** (100 mg, 0.36 mmol) or **1b** (200 mg, 0.76 mmol) and $[Co_2(CO)_8]$ (148 mg, 0.43 mmol or 400 mg, 1.17 mmol, resp.) in dry benzene (25 ml or 40 ml, resp.) was heated in a sealed tube at 80° for 22 h. The mixture was filtered and the residue washed with Et_2O . The filtrate was evaporated and the residue subjected to prep. TLC (5 or 10 plates, resp.; petroleum ether/AcOEt/acetone 10:1:1, twofold development). From the UV-active (254 nm) zone at larger R_f , after elution with $CHCl_3$, evaporation, and recrystallization from hexane, pure **3a** (58 mg, 64%) or **3b** (40 mg, 21%) were obtained. The product **3a** was shown to be identical (m.p., TLC, IR) with an authentic sample [2]. From the UV-active (254 nm) zone at smaller R_f following the same procedure, **1a** (32 mg, 32%) or **1b** (80 mg, 40%) were recovered. Parallel runs under the same conditions, but not using $[Co_2(CO)_8]$, showed only starting material.

*1-Ethyl-3,3-dimethyl-1H-benz[*g*]indol-2(3H)-one (3b).* M.p. 86.0–89.0°. IR ($CHCl_3$): 2965m, 2930m, 2865w, 1690s, 1620w. 1H -NMR (250 MHz, $CDCl_3$): 8.23 (*d*, $J = 7.0$, 1 arom. H); 7.85 (*d*, $J = 7.0$, 1 arom. H); 7.59 (*d*, $J = 7.0$, 1 arom. H); 7.44 (*t*, $J = 8.0$, H–C(7), H–C(8)); 7.36 (*d*, $J = 8.0$, 1 arom. H); 4.33 (*q*, $J = 6.8$, CH_2); 1.41 (*br. s*, 3 CH_3). ^{13}C -NMR (62.9 MHz, $CDCl_3$): 182.7 (*s*, C(2)); 151.3 (*s*, C(9b)); 134.4, 132.2, 120.8 (3*s*, C(3a), C(5a), C(9a)); 129.6, 126.0, 125.1, 123.2, 121.5, 120.1 (6*d*, C(4) to C(9)); 43.8 (*s*, C(3)); 37.1 (*t*, CH_2); 24.4 (*q*, 2 CH_3 –C(3)); 14.7 (*q*, CH_3CH_2). MS (70 eV): 240 (14), 239 (82, M^+), 225 (14), 224 (100, $M^+ - CH_3$), 196 (18), 180 (11), 178 (8), 167 (12), 152 (7).

3. *Thermal Reactions of 4 in the Presence of $[Co_2(CO)_8]$.* A soln. of **4a** (26 mg) in benzene (1 ml) was heated at reflux for 16 h. The solvent was evaporated and the residue containing N-(2,2-diphenylacetyl)-2-methyl-N,4,4-triphenylbuta-2,3-dienamide (**5**) analyzed (the signals of **4a** were subtracted): IR ($CHCl_3$): 1950m, 1685s, 1660m (sh), 1590m. 1H -NMR (250 MHz, $CDCl_3$): 6.82 (*s*, $CHPh_2$); 2.06 (*br. s*, CH_3).

A soln. of **4a** (520 mg, 1 mmol) and $[Co_2(CO)_8]$ (400 mg, 1.17 mmol) in dry benzene (10 ml) was heated in a sealed tube at 80° for 16 h. The mixture was filtered, the residue washed with Et_2O , and the filtrate evaporated. The residue was subjected to prep. TLC (7 plates; petroleum ether/AcOEt/acetone 10:1:1, twofold development). The pale yellow zone at R_f 0.5 was eluted with $CHCl_3$, the solvent evaporated, and the residue recrystallized from hexane/ CH_2Cl_2 to give pure N,2,2-triphenylacetamide (**6**; 124 mg, 38%), identical with an authentic sample (m.p., TLC, IR) [8].

4. *Photochemical Reactions of 1.* 4.1. *Direct Irradiation.* A soln. of **1a** (160 mg, 0.58 mmol) or **1b** (194 mg, 0.73 mmol) in cyclohexane (300 ml) was irradiated with a 15-W low-pressure Hg lamp under N_2 for 1 or 8 h, resp., the solvent evaporated, and the residue separated by prep. TLC (5 plates; above solvent system, fivefold development). The yellow zone was eluted with $CHCl_3$; **7a** (82 mg, 52%) as an oil or **7b** (38 mg, 20%) which was recrystallized from hexane/ Et_2O (yellow prisms). The colourless but UV-active (254 nm) zone was eluted with $CHCl_3$ to afford, after recrystallization from hexane/ Et_2O , recovered **1a** (60 mg, 38%) or **1b** (120 mg, 60%).

1-Benzyl-3,3-dimethyl-1H-cycloocta[b]pyrrol-2(3H)-one (7a). Orange oil. IR ($CHCl_3$): 2955m, 2915m, 2855w, 1690s, 1650m, 1630m, 1600w. 1H -NMR (250 MHz, $CDCl_3$): 7.4–7.1 (*m*, 5 arom. H); 5.92 (*dd*, $J = 11.0$, 4.5, H–C(5) or H–C(8)); 5.85 (*dd*, $J = 11.0$, 4.5, H–C(8) or H–C(5)); 5.72 (*dd*, $J = 11.0$, 4.0, H–C(6) or H–C(7)); 5.68 (*d*, $J = 11.0$, H–C(4) or H–C(9)); 5.60 (*dd*, $J = 10.5$, 4.5, H–C(7) or H–C(6)); 5.55 (*d*, $J = 11.0$, H–C(9) or H–C(4)); 4.63 (*s*, CH_2); 1.23 (*s*, 2 CH_3); irradiation at 5.88 (H–C(5) and H–C(8)) gave: 5.72 (*d*, $J = 11.0$, H–C(6) or H–C(7)), 5.68 (*s*, H–C(4) or H–C(9)), 5.60 (*d*, $J = 11.0$, H–C(7) or H–C(6)), and 5.55 (*s*, H–C(9) or H–C(4)). ^{13}C -NMR (62.9 MHz, $CDCl_3$): 182.8 (*s*, C(2)); 137.5 (*s*, C(9a)); 136.9 (*s*, C (arom.)); 137.2, 133.7, 132.8, 131.5, 128.6, 127.2, 126.8, 126.2 (8*d*, C(4) to C(9), 3 CH (arom.)); 122.5 (*s*, C(3a)); 47.5 (*s*, C(3)); 43.5 (*t*, CH_2); 22.8 (*q*, 2 CH_3). MS (70 eV): 277 (57, M^+), 262 (10, $M^+ - CH_3$), 251 (12), 249 (11, $M^+ - CO$), 158 (28), 91 (100, $PhCH_2^+$).

1-Ethyl-3,3-dimethyl-1H-benzo[7,8]cycloocta[1,2-b]pyrrol-2(3H)-one (7b). M.p. 131.5–133.0°. IR ($CHCl_3$): 2960m, 2920w, 2860w, 1685s, 1650m, 1610w. 1H -NMR (250 MHz, $CDCl_3$): 7.35–7.25 (*m*, 2 arom. H); 7.05–7.00 (*m*, 2 arom. H); 6.59 (*d*, $J = 11.5$, H–C(4) or H–C(7)); 6.04 (*dd*, $J = 11.5$, 3.5, H–C(5) or H–C(6)); 5.96 (*dd*, $J = 11.2$, 3.8, H–C(6) or H–C(5)); 5.87 (*d*, $J = 11.2$, H–C(7) or H–C(4)); 3.81 (*dq*, $J = 14.5$, 7.3, 1 H, CH_2); 3.15 (*dq*, $J = 14.5$, 7.3, 1 H, CH_2); 1.26 (*s*, CH_3); 1.18 (*s*, CH_3); 0.90 (*t*, $J = 7.3$, CH_3CH_2). ^{13}C -NMR (62.9 MHz, $CDCl_3$): 183.8 (*s*, C(2)); 140.0, 137.3, 131.8 (3*s*, C(3a), C(8), C(9), C(9a)); 132.9, 132.7, 131.5, 129.9, 129.2, 128.6, 126.9, 125.6 (8*d*, C(4) to C(7), CH (arom.)); 47.8 (*s*, C(3)); 35.1 (*t*, CH_2); 23.3, 21.8 (2*q*, 2 CH_3); 13.2 (*q*, CH_3CH_2). MS (70 eV): 266 (18), 265 (100, M^+), 250 (36, $M^+ - CH_3$), 237 (21, $M^+ - CO$), 222 (44), 208 (12), 194 (33), 180 (20), 179 (27), 167 (15), 165 (16), 153 (18), 152 (16).

The irradiation of **1a, b** in the presence of $[\text{Co}_2(\text{CO})_8]$ under the same conditions was shown, by TLC, to give the same photoproducts **7a** and **7b**.

4.2. Irradiation in the Presence of $[\text{Fe}(\text{CO})_5]$. A soln. of **1a** (260 mg, 0.94 mmol) or **1b** (280 mg, 1.06 mmol) and $[\text{Fe}(\text{CO})_5]$ (2 ml) in cyclohexane (300 ml) was irradiated with a 50-W high-pressure Hg lamp (*Solidex* filter) under N_2 for 1 h. The solvent was evaporated and the residue separated by TLC (7 plates; petroleum ether/AcOEt/acetone 10:1:1, threefold development). The yellow zone at larger R_f in the case of **1a** was shown to contain an unstable complex (elution with CHCl_3). From the yellow zone at smaller R_f , after elution and recrystallization from hexane/ Et_2O , **8** (63 mg, 15%) was obtained, contaminated with **1a**. In the case of **1b**, the yellow zone gave, after usual workup and recrystallization from hexane/ Et_2O , **9** (48 mg, 12%) as yellow crystals, m.p. 187.0–188.0°. From the colourless but UV-active (254 nm) zone, starting **1b** (94 mg, 33%) was recovered.

(*2-Benzyl-4,4-dimethyl-2-azatricyclo[5.2.2.0^{1,3}]undeca-5,8,10-trien-3-one*)tricarboxyliron (**8**). IR (CHCl_3): 2980m, 2960m, 2920m, 2860w, 2025vs, 1965vs, 1940vs, 1680s, 1660s, 1585w. $^1\text{H-NMR}$ (250 MHz, CDCl_3): 7.61 (*d*, $J = 7.8$, 2 arom. H); 7.4–7.2 (*m*, 3 arom. H); 6.12 (*d*, $J = 5.5$, H–C(6)); 5.13 (*s*, CH_2); 4.03 (*m*, H–C(7)); 3.08 (br. *s*, H–C(8), H–C(9), H–C(10), H–C(11)); 1.28 (*s*, 2 CH_3). $^{13}\text{C-NMR}$ (62.9 MHz, CDCl_3): 215.8 (*s*, Fe–CO); 45.8, 44.6 (*2d*, C(8), C(9), C(10), C(11)); 26.3 (*q*, CH_3); remaining signals, overlapped with the signals of **1a**. MS (70 eV): 417 (1, M^+), 389 (0.2, $M^+ - \text{CO}$), 361 (22, $M^+ - 2 \text{CO}$), 333 (68, $M^+ - 3 \text{CO}$), 307 (100, $M^+ - \text{C}_2\text{H}_4 - 3 \text{CO}$), 305 (7), 277 (3, $M^+ - \text{Fe}(\text{CO})_3$), 216 (12), 91 (40, PhCH_2^+).

(*[1RS,7SR]-2-Ethyl-4,4-dimethyl-2-azabenzof[8,9]tricyclo[5.2.2.0^{1,5}]undeca-5,8,10-trien-3-one*)tricarboxyliron (**9**). M.p. 187.0–188.0°. IR (CHCl_3): 2965m, 2925m, 2865m, 2025vs, 1965vs, 1950vs (sh), 1675s, 1595w. $^1\text{H-NMR}$ (250 MHz, CDCl_3): 7.25–7.10 (*m*, 4 arom. H); 4.87 (*t*, $J = 6.0$, H–C(7)); 4.25 (*dq*, $J = 15.0$, 7.2, 1 H, $\text{CH}_3\text{CH}_2\text{N}$); 3.68 (*t*, $J = 6.0$, H–C(11)); 3.58 (*dq*, $J = 15.0$, 7.2, 1 H, $\text{CH}_3\text{CH}_2\text{N}$); 3.35 (*d*, $J = 5.5$, H–C(10)); 3.12 (*d*, $J = 6.0$, H–C(6)); 1.65 (*t*, $J = 7.2$, CH_3CH_2); 1.10 (*s*, CH_3); 0.63 (*s*, CH_3). $^{13}\text{C-NMR}$ (62.9 MHz, CDCl_3): 215.9 (*s*, Fe–CO); 179.4 (*s*, C(3)); 145.2, 144.5 (*2s*, C(8), C(9)); 126.7, 126.6, 121.7, 119.9 (*4d*, CH (arom.)); 73.3 (*s*, C(1)); 68.7 (*s*, C(5)); 50.6 (*d*, C(7)); 45.2, 43.5 (*2d*, C(10), C(11)); 43.4 (*s*, C(4)); 30.7 (*d*, C(6)); 28.7, 25.0 (*2q*, 2 CH_3 –C(4)); 14.8 (*q*, C_2H_5). MS (70 eV): 405 (2, M^+), 377 (11, $M^+ - \text{CO}$), 349 (48, $M^+ - 2 \text{CO}$), 321 (100, $M^+ - 3 \text{CO}$), 293 (20), 277 (12), 265 (21, $M^+ - \text{Fe}(\text{CO})_3$), 250 (15), 56 (30).

5. Irradiation of 4 in the Presence of $[\text{Fe}(\text{CO})_5]$. A soln. of **4a** (200 mg, 0.38 mmol) and $[\text{Fe}(\text{CO})_5]$ (3 ml) in dry THF (250 ml) was irradiated with a 50-W high-pressure Hg lamp under N_2 through *Solidex* filter for 3 h. The solvent was evaporated and the residue separated by prep. TLC (10 plates; above system). From the colourless zone, after usual workup, **4a** (48 mg, 24%) was recovered. The yellow zone was treated as usually to give crude [*2-(2,2-diphenylacetyl)-4-methyl-6,6-diphenyl-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one*]tricarboxyliron (**11**; 112 mg, 44%) as yellow crystals, m.p. 100.0–105.0° (dec.), which was shown to be pure by TLC and was not recrystallized. IR (CHCl_3): 2915m, 2880m, 2830w, 2815w, 2055vs, 1985vs (br.), 1735s, 1695w, 1625w. $^1\text{H-NMR}$ (250 MHz, CDCl_3): 7.56 (*d*, $J = 7.0$, 4 arom. H); 7.4–7.0 (*m*, 16 arom. H); 6.95 (*s*, CHCO); 3.98 (*t*, $J = 5.0$, H–C(7)); 3.12 (*d*, $J = 5.0$, H–C(9), H–C(10)); 2.80 (*t*, $J = 5.0$, H–C(8), H–C(11)); 1.30 (*s*, CH_3). $^{13}\text{C-NMR}$ (62.9 MHz, CDCl_3): 214.7 (*s*, Fe–CO); 171.9, 170.8 (*2s*, C(3), CHCON); 163.2 (*s*, C(5)); 139.6, 138.9 (*2s*, 2 C (arom.)–C(6), 2 C (arom.)–CH); 129.2, 128.4, 128.3, 127.9, 127.1, 127.0 (*6d*, CH (arom.)); 125.0 (*s*, C(4)); 67.0 (*s*, C(1)); 58.1 (*s*, C(6)); 56.0 (*d*, CHCO); 49.4 (*d*, C(7)); 41.7, 40.2 (*2d*, C(8), C(9), C(10), C(11)); 9.9 (*q*, CH_3). MS (70 eV): 603 (2, $M^+ - 2 \text{CO}$), 575 (3, $M^+ - 3 \text{CO}$), 547 (5), 519 (5, $M^+ - \text{Fe}(\text{CO})_3$), 325 (18), 310 (12), 234 (18), 205 (16), 194 (37, $\text{Ph}_2\text{C}=\text{C}=\text{O}^+$), 168 (62), 167 (100, Ph_2CH^+), 165 (70).

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