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Rhodium(II)-Catalyzed Decomposition of 1-Diazo-4-(2-naphthyl)butan-2-one. Direct Chemical Evidence for the Formation of the Norcaradiene System in the Intramolecular Buchner Reaction

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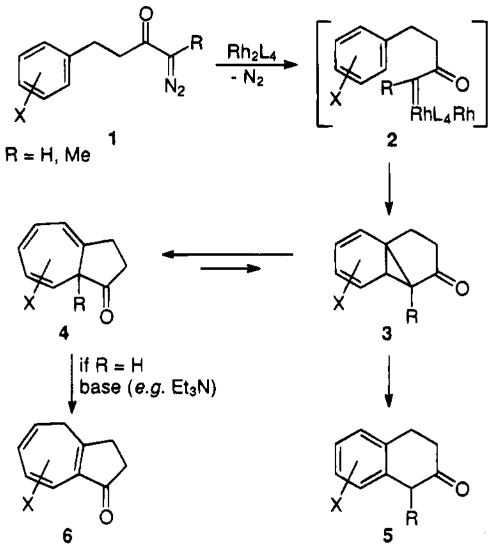
The dirhodium(II)-catalyzed decomposition of 4-aryl-1-diazobutan-2-ones (**1**, R = H) and 5-aryl-2-diazopentan-3-ones (**1**, R = Me) is commonly described as cycloaddition of the metal-stabilized α-ketocarbene (**2**)[1] to the aromatic nucleus to form a tricyclo[5.3.0.$0^{1,6}$]deca-2,4-dien-8-one (**3**) which rapidly rearranges to a 3,8a-dihydroazulen-1(2*H*)-one (**4**)[2] (Scheme 1).

McKervey suggested the existence of a norcaradiene (**3**)−cycloheptatriene (**4**) equilibrium, the bicyclic component **4** being strongly dominant at room temperature except when a methyl group is present at the bridgehead carbon (**4**, R = Me).[3,4] On this assumption the following findings could well be explained: (i) β-tetralones (**5**) are obtained in high yields after addition of catalytic amounts of TFA to the crude product of the intramolecular Buchner reaction (or directly if the aromatic ring of the starting α-diazoketone bears an electron-donating group at the *meta*-position);[3a,b,d,f,5] (ii) treatment of the crude product of the same reaction with bases, (*e.g.*, triethylamine) furnishes cross-conjugated dihydroazulenones (**6**).[3a,d,5]

The occurrence of the norcaradiene derivative has been supported in particular instances by spectroscopic evidence[3b−e,6] or by chemical interception,[6] *i.e.*, in the case of tautomeric equilibrium mixtures arising from decomposition of α-diazoketones methyl substituted at the diazo carbon atom (**1**, R = Me). However, neither the direct characterization of a tricyclo[5.3.0.$0^{1,6}$]decadienone (**3**) as first intermediate in the intramolecular cyclopropanation of the benzene ring nor an unequivocal proof of its acid-catalyzed conversion into the corresponding β-tetralone have been reported so far.[2e] We thought the isolation of such a norcaradiene-like valence tautomer to be possible provided that the cycloreversion reaction of the tricyclic framework would be thermodynamically and/or kinetically disfavored, *e.g.*, by a concomitant dearomatization.

Scheme 1



1-Diazo-4-(2-naphthyl)butan-2-one (**7c**)[7] was prepared from 3-(2-naphthyl)propionic acid (**7a**)[8] *via* the standard procedure of conversion to the acyl chloride (**7b**) followed by treatment with etheral diazomethane.[3d,9] The diazoketone **7c** was then added to a boiling solution of rhodium(II) diacetate dimer in dichloromethane using the glass apparatus described to achieve high dilution reaction conditions.[9] The decomposition of **7c**, which could be monitored by TLC,[10] was complete within 5 h.[11] The main reaction product was shown to be tetracyclo[9.3.0.$0^{1,10}$.$0^{4,9}$]tetradeca-2,4,6,8-tetraen-12-one (**8**) (71% isolated yield) on the basis of the following spectral data: UV λ_{max} (log ϵ) (MeOH) 228 (4.35), 272 (3.94), 308 (3.39) nm; IR (KBr) 1707 cm^{-1}; EIMS *m*/*e* 196 (M^+, 76), 168 (100); for ^1H and ^{13}C NMR see Table 1. In particular, the *cis*-junction involving the cyclopropane ring with the six-[12] as well as the five-membered ring was consistent with the high field chemical shift of H-11[13] and with the

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(1) Leading papers on dirhodium(II) carbene reactions: (a) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919−939. (b) Doyle, M. P. *Acc. Chem. Res.* **1986**, *19*, 348−356. (c) Padwa, A.; Austin, D. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1797−1815.

(2) Leading papers on the intramolecular carbenoid reactions: (a) Maas, G. *Top. Curr. Chem.* **1987**, *137*, 75−253. (b) Adams, J.; Spero, D. M. *Tetrahedron* **1991**, *47*, 1765−1808. (c) Padwa, A.; Krumpe, K. E. *Tetrahedron* **1992**, *48*, 5385−5453. (d) Padwa, A.; Austin, D. J.; Price, A. T.; Semones, M. A.; Doyle, M. P.; Protopopova, M. N.; Winchester, W. R.; Tran, A. *J. Am. Chem. Soc.* **1993**, *115*, 8669−8680. (e) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091−1160.

(3) (a) McKervey, M. A.; Tuladhar, S. M.; Twohig, F. M. *J. Chem. Soc., Chem. Commun.* **1984**, 129−130. (b) Kennedy, M.; McKervey, M. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1028−1030. (c) Duddeck, H.; Kennedy, M.; McKervey, M. A.; Twohig, F. M. *J. Chem. Soc., Chem. Commun.* **1988**, 1586−1588. (d) Kennedy, M.; McKervey, M. A.; Maguire, A. R.; Tuladhar, S. M.; Twohig, M. F. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1047−1054. (e) Kennedy, M.; McKervey, M. A. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2565−2574. (f) Duddeck, H.; Ferguson, G.; Kaitner, B.; Kennedy, M.; McKervey, M. A.; Maguire, A. R. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1055−1063.

(4) On the influence of substituents on the position of the norcaradiene−cycloheptatriene equilibrium see also: Hannemann, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 284−285 and references cited therein.

(5) Cordi, A. A.; Lacoste, J.-M.; Hennig, P. *J. Chem. Soc., Perkin Trans. 1* **1993**, 3−4.

(6) Saba, A. *Tetrahedron Lett.* **1990**, *31*, 4657−4660.

(7) All new compounds gave satisfactory elemental analyses. **7c**: IR (KBr) 2120, 1626 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.15 (s, 1H, $-CHN_2$); ^{13}C NMR ($CDCl_3$) δ54.58 ($-CHN_2$), 193.73 (C=O).

(8) It was prepared by sequential condensation of 2-naphthaldehyde with malonic acid and Pd/C hydrogenation of the resulting 3-(2-naphthyl)acrylic acid according to a known procedure: Copinga, S.; Tepper, P. G.; Grol, C. J.; Horn, A. S.; Dubocovich, M. L. *J. Med. Chem.* **1993**, *36*, 2891−2898.

(9) Scott, L. T.; Sumpter, C. A. *Organic Syntheses*; Wiley: New York, 1990; Vol. 69, pp 180−187.

(10) *n*-Hexane−EtOAc (2:1). This eluent was used for all TLC and flash chromatography separations reported here.

(11) Typical experiment: a solution of **7c** (5 g) in CH_2Cl_2 (30 mL) was added dropwise to $Rh_2(OAc)_4$ (30 mg) in CH_2Cl_2 (100 mL) through of a "trident" reservoir.[9] After heating to a reflux for 5 h under N_2, the reaction mixture was cooled, washed with water, dried, and evaporated under reduced pressure. The orange oil residue (3.8 g) was flash chromatographed (SiO_2, 500 g)[10] to give **8** (3.1 g) which was found to be pure by TLC (R_f 0.68). Recrystallization from ether afforded pale yellow crystals, mp 73−75 °C. All mps are uncorrected.

(12) In principle, a *trans*-junction in a bicyclo[4.1.0]hexane is possible; see, for example: Paukstelis, J. V. ; Kao, J. *J. Am. Chem. Soc.* **1972**, *94*, 4783−4784.

(13) Typical chemical shifts for protons at the angular α-position to the carbonyl group in bicyclo[3.1.0]hexan-2-ones are in the range δ 1.7−2.0; see, for example: (a) Srikrishna, A.; Krishnan, K. *Tetrahedron* **1992**, *48*, 3429−3436. (b) Murai, A.; Kato, K.; Masamune, T. *Tetrahedron Lett.* **1982**, *23*, 2887−2890. Thus, the upfield shift for the H-11 resonance in **8** is understandable if one assumes a *cis* six−three fusion causing a marked diamagnetic shielding of that proton. Vogel, E.; Wendisch, D.; Roth, W. R. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 443.

0022-3263/95/1960-0484$09.00/0

Table 1. NMR Data for Compound 8[a]

carbon no.	δ ^{1}H[b]	δ ^{13}C[c]
1		38.41
2	6.20, d, $J = 9.6$ Hz	127.99
3	6.41, d, $J = 9.6$ Hz	125.41
4		131.19
5, 6, 7	7.15–7.23, m	126.86, 127.61, 127.99
8	7.35–7.39, m	128.24
9		131.77
10	3.03, d, $J = 2.6$ Hz	35.01
11	0.76, d, $J = 2.6$ Hz	32.63
12		214.15
13, 14	2.20–2.44, m	27.96, 32.91

[a] Recorded in $CDCl_3$. [b] 300 MHz. [c] 75.47 MHz. Assignments were based on DEPT, HETCOR, COLOC (7 Hz), and ^{1}H NOE difference experiments.

value of the coupling constant observed for H-10 and H-11 (Table 1).[14]

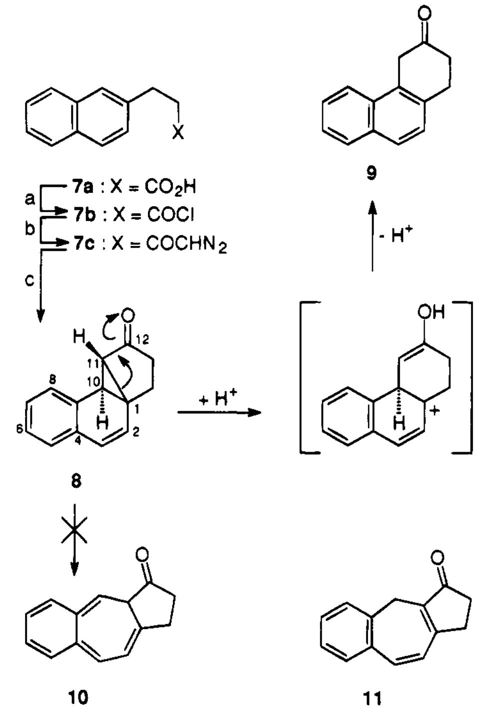
When catalytic amounts of TFA were added to a dichloromethane solution of **8** at rt the almost immediate formation of a new compound, *i.e.*, 1,2-dihydrophenanthren-3(4*H*)-one (**9**), was observed in TLC.[15] By contrast, compound **8** was recovered quantitatively after treatment with triethylamine in dichloromethane for 1 h under reflux. The rearrangement of **8** to **9** can be interpreted assuming the intermediacy of an acid-induced enolization as shown in Scheme 2.[16]

The chromatographic purification of the crude product coming from Rh(II)-induced decomposition of **7c** afforded, besides compound **8**, a more polar substance (R_f 0.57). The structure of 1,10-dihydrobenzo[*f*]azulen-3(2*H*)-one (**14**) was assigned to this byproduct (8% isolated yield) in view of its spectral data.[17]

In particular, the NOE interaction between H-1 and H-10 provided the most convincing evidence for ruling out the isomeric structure **11** (0.6% enhancement of the H-10 signal by irradiation of H-1; 1.4% and 4.8% intensity enhancement of H-1 and H-9, respectively, by irradiation of H-10). It should be noted that the occurence of compound **11** resulting from a double bond movement in the ketone **10** was to be considered since a dynamic equilibrium between **10** and the more stable tautomer **8** at the reaction temperature could not be excluded *a priori*.

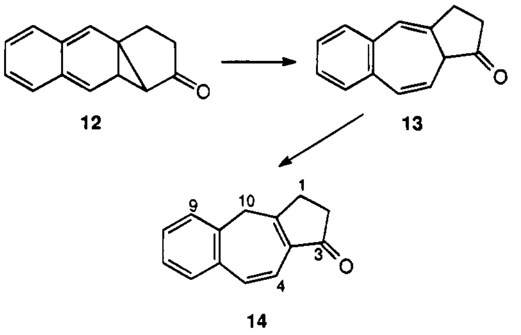
The formation of **14** can be explained in terms of an attack of the carbenoid carbon of **7c** on the 2,3-side of the naphthalene nucleus followed by double bond migration in the tricyclic nonconjugated ketone **13** (Scheme 3). Aromatization is clearly the driving force for the cycloreversion of the norcaradiene system of **12** to give the dihydroazulenone **13**.

Scheme 2[a]



[a] Key: (a) $(COCl)_2$; (b) CH_2N_2; (c) $Rh_2(AcO)_4$.

Scheme 3



The ratio **8**:**14** in the reaction mixture after complete decomposition of the diazoketone **7c**, when estimated by HPTLC,[18] was found to be *ca.* 7.6, a value which is the expression of the regioselectivity in the attack of the rhodium(II)-stabilized α-keto carbene on the naphthalene nucleus.

In conclusion, the isolation of compound **8** and its quantitative acid-catalyzed conversion into **9** represent the first direct chemical evidence for the intermediacy of a norcaradiene-like species toward the typical products of the intramolecular Buchner reaction.

Acknowledgment. Thanks are due to MURST (Italy) for financial support.

Supplementary Material Available: Experimental procedures and copies of IR, EIMS, and ^{1}H and ^{13}C NMR spectra for compounds **7c**, **8**, **9**, and **14** (19 pages).

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[14] Coupling constants for *cis* vicinal protons in cyclopropane rings, including fused systems, are never smaller than 7.0 Hz (and always larger than J_{trans}): Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon Press: Oxford, 1969; pp 286–287. See also ref 13a.

[15] **9**: 98% isolated yield; mp 70–71 °C from ether; R_f 0.78; UV λ_{max} (log ϵ) (MeOH) 228 (4.31), 282 (3.51) nm; IR (KBr) 1708 cm^{-1}; EIMS 196 (M^+, 81), 167 (35), 154 (100); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.71 (app t, $\langle J \rangle = 6.9$ Hz, 2H, H_2-2), 3.24 (app t, $\langle J \rangle = 6.9$ Hz, 2H, H_2-1), 3.92 (s, 2H, H_2-4), 7.32 (d, $J = 8.4$ Hz, 1H, H-10), 7.45–7.56 (m, 2H, H-6, H-7), 7.72 (d, $J = 8.4$ Hz, 1H, H-9), 7.80–7.86 (m, 2H, H-5, H-8); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 29.57 (C-1), 38.74 (C-2), 40.31 (C-4), 122.29, 128.65 (C-5, C-8), 125.41, 126.55 (C-6, C-7), 126.55 (C-10), 127.03 (C-9), 128.25, 131.43, 132.40, 133.23 (C-4a, C-4b, C-8a, C-10a), 209.93 (C-3). Assignments based on HETCOR and ^{1}H NOE experiments.

[16] Wong, H. N. C.; Hon, M.-Y.; Tse, C.-W.; Yip, Y.-C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165–198.

[17] **14**: mp 112–113 °C from ether; R_f 0.57; UV λ_{max} (log ϵ) (MeOH) 238 (4.30), 268 (3.97) nm; IR (KBr) 1695, 1634 cm^{-1}; EIMS 196 (M^+, 100), 168 (40), 154 (98); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.47 (m, 2H, H_2-2), 2.78 (m, 2H, H_2-1), 3.49 (s, 2H, H_2-10), 6.70 (d, $J = 11.3$ Hz, 1H, H-4), 7.07 (d, $J = 11.3$ Hz, 1H, H-5), 7.18 (d, $J = 7.3$ Hz, 1H, H-9), 7.25–7.35 (m, 3H, H-6, H-7, H-8); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 30.04 (C-1), 35.39 (C-2), 38.19 (C-10), 120.62 (C-4), 128.41 (C-9), 126.56, 129.15 (C-6, C-7, C-8), 133.91 (C-5), 133.38, 136.16 (C-3a, C-5a, C-9a), 170.08 (C-10a), 205.30 (C-3). Assignments based on HETCOR and ^{1}H NOE experiments.

[18] A Camag TLC Scanner II was used at 254 nm. Calibration curves were obtained for both compounds examined.