Bimolecular Formation of Radicals by Hydrogen Transfer, 11[◇]

Transfer Hydrogenation of Conjugated Cyclic Dienes and Trienes

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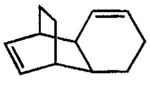
1,3-Cyclohexadiene, 1,3-cycloheptadiene and cycloheptatriene are smoothly hydrogenated to cyclohexene and cycloheptene, respectively, when heated to 260–340 °C with an excess of 9,10-dihydroanthracene (DHA) in diphenyl ether or benzonitrile. On the basis of a mechanistic study a nonchain three-step mechanism is proposed which is initiated by a transfer of a hydrogen atom from DHA to the polyenes (retrodisproportionation).

In previous publications[1] it was shown, that phenyl-substituted alkenes[2], azoarenes[3,4], aromatic nitro and nitroso compounds[3] as well as quinones[5] are hydrogenated when they are heated with efficient hydrogen donors like 9,10-dihydroanthracene (DHA) without the addition of a catalyst. The reaction temperature varies between room temperature (certain quinone reactions)[5] and ca. 300 °C (α-methylstyrene and DHA)[2]. Mechanistic investigations indicate that the first step of these reactions is an H-atom transfer process, e.g.

$$\mathrm{A{-}H + B{=}C \xrightarrow{T} A^{\bullet} + HB{-}C^{\bullet}}$$

This rather novel transformation[1] was called “retrodisproportionation” because the reverse reaction is the well-known termination reaction of radicals, the radical disproportionation[6]. Retrodisproportionations are examples of bimolecular radical formations which were summarized as MIRF reactions (molecule-induced radical formation) by Pryor[7,8]. In this paper transfer hydrogenations of the cyclic polyenes 1,3-cyclohexadiene (**4**), 1,3-cycloheptadiene (**10**) and cycloheptatriene (**12**) with 9,10-dihydroanthracene (DHA) are reported.

When 1,3-cyclohexadiene (**4**, 0.08 M) and DHA (1.00 M) were heated at 260–350 °C in degassed diphenyl ether for 20–100 min. the expected products cyclohexene (**7**) and anthracene (**9**) were detected by GC/MS (see Scheme 1) as well as four minor products, to which the following structures were tentatively assigned on the basis of GC/MS analyses: tricyclo[6.2.2.0^{2,7}]dodeca-1,9-diene **1**, the Diels-Alder dimer of 1,3-cyclohexadiene (**4**, 15%)[9], tricyclo[6.2.2.0^{2,7}]dodeca-9-ene (**2**, 8%)[10] the Diels Alder adduct of cyclohexene (**7**) and cyclohexadiene (**4**), tetrahydrotriptycene (**3**, 12%), the Diels-Alder adduct of cyclohexene (**7**), and anthracene (**9**)[11] and benzene (25%).



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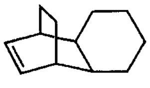

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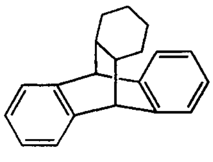

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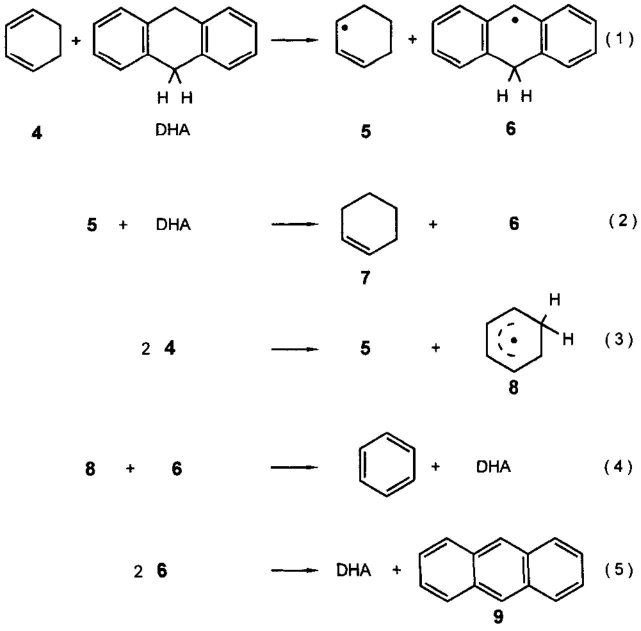
The retrodisproportionation reactions (1) and (3)[12] followed by reactions (2), (4) and (5) seem to be responsible for the formation of cyclohexene (**7**) and benzene.

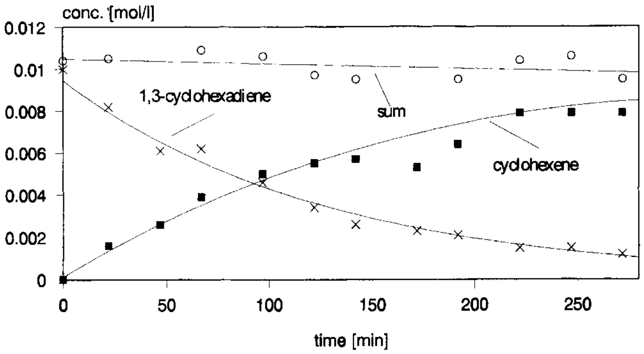
Scheme 1. Mechanism of transfer hydrogenation of cyclohexadiene **4** (for experimental conditions see Table 1)



[◇] For part 10 see: Ref.[5].

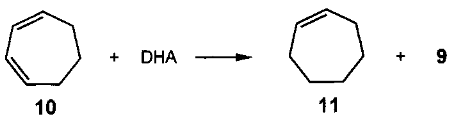
In order to reduce the rates of the competing Diels-Alder reactions and the self-retrodisproportionation (3) of **4** the reactions were conducted at a lower concentration of **4** (0.01 M) and a higher concentration of DHA (2.00 M). Under these conditions at 260–300 °C no Diels-Alder adducts were observed and only 5% of benzene were detected, besides almost quantitative formation of cyclohexene (**7**). In Figure 1 the time dependence of the concentration of **4** and cyclohexene (**7**) is shown.

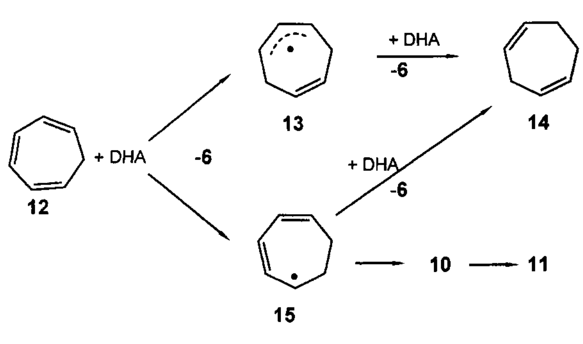
Figure 1. Mass balance of the reduction of 1,3-cyclohexadiene **4**, (0.01 M) to cyclohexene **7** with 9,10-dihydroanthracene (DHA, 2.00 M) in diphenyl ether at 290 °C



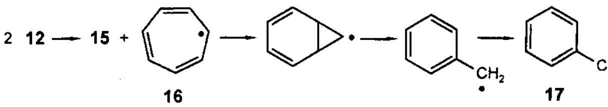
The transfer hydrogenation of 1,3-cycloheptadiene (**10**) with DHA at 290–340 °C produced cycloheptene (**11**) and anthracene (**9**) in 90% yield by a reaction series corresponding to eqs. (1), (2) and (5). Even at a higher concentration of **10** (0.08 M) and DHA (1.00 M) than used above for **4** no significant yield of side products was detected.

When cycloheptatriene (**12**) (0.08 M) was allowed to react with DHA (1.00 M) under transfer hydrogenation conditions (280–320 °C) in diphenyl ether 1,3-cycloheptadiene (**10**) was detected as an intermediate and cycloheptene (**11**) and anthracene (**9**) were the main products besides 25% of toluene (**17**) and 8% of 1,4-cycloheptadiene (**14**). **14** could be formed either by non-regioselective H-atom transfer from DHA to **12** or to the valence isomer norcaradiene or by exclusive formation of the radicals **15** and their non-regioselective trapping by DHA.





Unexpectedly, no 1,4-cycloheptadiene (**14**) was formed when the transfer hydrogenation of **12** was performed at a lower concentration of **12** (0.01 M) and a higher concentration of DHA (2.00 M). Possibly, **14** is the product of disproportionation of radicals **13** which comes into play only at low DHA concentrations. The yield of toluene (**17**) is also reduced to 1–7% under these conditions, decreasing with increasing temperature. **17** is possibly formed according to eq. (6) by retrodisproportionation of two molecules of **12**[12] and rearrangement of the intermediate cycloheptatrienyl radicals **16**. Another mechanism following first-order kinetics was proposed previously for the formation of toluene from cycloheptatriene (**12**) at 300 °C[13]. The fact, that the yield of toluene is reduced at lower concentration supports eq. (6) but does not exclude the former explanation[13], because the rate of the competing second-order retrodisproportionation is increased at higher DHA concentrations.



(6)

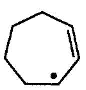
Attempts to reduce 1,3-cyclooctadiene or cyclooctatetraene by transfer hydrogenation at 300 °C gave multicomponent hydrogenation products and side products which were not further analyzed. The known thermal reorganization reactions of these compounds must be responsible for this[13].

Table 1. Transfer hydrogenation of 1,3-cyclohexadiene **4** (0.01 M), 1,3-cycloheptadiene **10** (0.08 M) and cycloheptatriene **12** (0.01 M) with 9,10-dihydroanthracene (DHA)[a] in degassed diphenyl ether (DE; E_T = 35.3[17b]) or benzonitrile (BN; E_T = 41.5[17b]); mass balances ≈90%

	Solvent	T[°C][b]	$10^5 \cdot k_2$ $M^{-1} \cdot s^{-1}$	± σ %	k_H/k_D	
4	DE	260.0	4.45	3.3		
	DE	270.0	7.43	3.3		$\Delta G^{\ddagger} = 43.4 \pm 0.3$ kcal/mol
	DE	280.0	12.72	2.4		$\Delta H^{\ddagger} = 29.7 \pm 0.3$ kcal/mol
	DE	290.0	20.33	3.8		$\Delta S^{\ddagger} = -23.9 \pm 0.6$ cal/° · mol
	DE	299.5	32.94	2.2		$\Delta H_R = 37.5$ kcal/mol
	DE[d]	300.0	18.45	4.1	1.79 (300°C)	
	BN	300.0	33.28	2.7		
10	DE	290.0	3.53	1.6		$\Delta G^{\ddagger} = 45.4 \pm 0.3$ kcal/mol
	DE	320.0	15.62	1.8		$\Delta H^{\ddagger} = 31.2 \pm 0.3$ kcal/mol
	DE	330.0	23.69	2.7		$\Delta S^{\ddagger} = -24.7 \pm 0.4$ cal/° · mol
	DE	340.0	37.44	1.6		$\Delta H_R = 39.4$ kcal/mol
	DE	351.0	59.45	3.6		
	DE[d]	340.0	17.01	3.8	2.20 (340°C)	
	BN	340.0	32.87	1.8		
12	DE	279.0	4.10	3.2		$\Delta G^{\ddagger} = 44.4 \pm 1.1$ kcal/mol
	DE	290.0	7.64	2.5		$\Delta H^{\ddagger} = 31.8 \pm 1.1$ kcal/mol
	DE	299.0	11.83	3.6		$\Delta S^{\ddagger} = -22.0 \pm 1.9$ cal/° · mol
	DE	310.0	21.69	2.3		$\Delta H_R = 39.4$ kcal/mol
	DE	320.0	33.58	3.6		
	DE[d]	310.0	10.96	2.2	1.98 (310°C)	
	BN	310.0	22.38	2.7		

[a] For **4** and **12**: DHA (2.00 M); for **10**: DHA (1.00 M). – [b] ±0.5 °C. – [c] Corrected for volume expansion during heating from 25 °C to the reaction temperature. – [d] [D_4]DHA.

The disappearance of **4**, **10** and **12** and the appearance of **7** and **11** (from **10**) followed second-order kinetics in agreement with a rate-determining retrodisproportionation step (1)[1,2]. When 9,9′,10,10′-tetradeuterio-9,10-dihydroanthracene ([D_4]DHA) was used as deuterium donor[2,12] and the transfer deuterations were interrupted after about 50% of **4**, **10** and **12** had been consumed, then no deuterium was incorporated into the residual H acceptors. This proves that the retrodisproportionation step (1) and the analogous H-atom transfers to **10** and **12** are irreversible under the chosen reaction conditions. The observation of deuterium isotope effects $k_H/k_D \approx 2$[1–4,12], which are close to the maximally possible value[14], supports the transfer of H in the rate-determining step. The rates, isotope effects and activation parameters for the transfer hydrogenations of **4**, **10** and **12** with DHA and [D_4]DHA are compiled in Table 1. At 290°C the rate ratio of **10** : **12** : **4** = 1 : 2.2 : 5.8 which is due mainly to small differences in the activation enthalpies $\Delta H^{\neq}$, $\Delta\Delta S^{\neq}$ being negligible in this series. The higher rate of consumption of **12** compared with that of **10** can be rationalized by the higher resonance energy of the cyclic pentadienyl radical **15** than that of the corresponding allyl radical **18** although it is not known if the H atom is transferred to the non-planar cycloheptatriene **12**[15] or to the norcaradiene valence isomer[16]. The higher rate of the reaction of **4** than those of **10** and **12** must be due to the slightly different stereoelectronic situation.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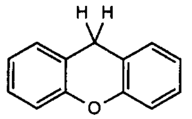
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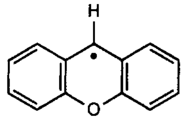
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The small solvent effects[17] on the rates listed in Table 1 support the H-atom transfer in contrast to a hydride-transfer mechanism because in the latter an ion pair would be formed. EPR was used to obtain additional evidence for the formation of radical intermediates. 9-Hydroanthryl radicals **6** could not be detected, in agreement with previous[1–3,5] reports for other examples. The short life time of these radicals, due to their fast disproportionation eq. (5), is probably responsible for this. Therefore, we used, as before[1,2,4], xanthene **19** as hydrogen donor and successfully obtained a strong signal of 9-xanthyl radicals **20** from the very beginning of the reaction and with similar intensity during the whole course of the reaction of **19** with **4** at 270°C in diphenyl ether. 9-Xanthyl radicals **20** cannot disproportionate and they are in equilibrium with their dimer under the reaction conditions[18].

As a final test for the retrodisproportionation step (1) the activation enthalpies $\Delta H^{\neq}$ were compared with the reaction enthalpies ΔH_R of the retrodisproportionation reactions (1) (see Table 1). They were obtained from thermochemical data or by computational methods (see Experimental) and are compiled in Table 1. In all three examples ΔH_R is 8 kcal/mol larger than $\Delta H^{\neq}$ which seems to be in contrast to Benson's concept[19] of thermochemical kinetics. It was suggested in another context[1], however, that the transition state of a retrodisproportionation step is due to a $\Delta G^{\neq}$ barrier and does not necessarily follow the reaction coordinate in ΔH. Because of the large negative $\Delta S^{\neq}$ values of these reactions the $\Delta G^{\neq}$ transition state does not geometrically coincide with the two radicals which are finally generated in the H-transfer step. In the $\Delta G^{\neq}$ transition-state the hydrogen atom is, accordingly, located somewhere between the two carbon atoms which are taking part in the reaction. The highest enthalpy $\Delta H^{\neq}$ has not yet been reached at this point. This model of the transition state also explains the observation of large isotope effects k_H/k_D as listed in Table 1. It requires that the migrating H atom is between the two reaction centers at the transition state and has not yet reached the terminal carbon atoms[14].

In summary, the first examples of retrodisproportionations or uncatalyzed hydrogen transfer-reactions of dienes and trienes have been reported. Previously, only aryl-substituted alkenes were exposed to this reaction successfully in the temperature range below 300°C[20]. From the synthetic point of view the transformation of conjugated dienes or trienes into alkenes is an interesting alternative to the reduction of dienes under conditions of the Birch reaction[21].

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Experimental

General: ^1H NMR: Bruker WM 250. – IR: Perkin-Elmer 398. – GC: Carlo-Erba fractometer GC 6000, Vega Series 1 and 2 with FID; Carlo-Erba Autosampler CTC-A 200; capillary columns: SE 54, 25 m (inner diameter: 0.32 mm; film thickness: 1 µm), DB 23, 30 m (inner diameter: 0.32 mm; film thickness: 0.25 µm), SE 54, 10 m (inner diameter: 0.32 mm; film thickness: 1 µm), DB 1, 25 m (inner diameter: 0.32 mm; film thickness: 0.25 µm), N_2 flow 2 ml/min. – Integrator 3390 A and 3392 A, Hewlett-Packard. – GC MS: Finnegan MAT 44 S, coupled to GC fractometer 3700, Varian. – Thermolysis: Tin thermostat (constructed in the laboratory[22]); electronic temperature control unit: DTC 2/CK 01, Oxford Electronic Instruments; temperature measurement: Pt 100/S 1220, Systemtechnik AB. – EPR: BER-420, Bruker. – Melting points: Apparatus Dr. Tottoli, Büchi (uncorrected values).

GC Conditions: System **4**/DHA: SE 54, 25 m; temperature program: 80°C (7 min) – 10°C/min – 250°C (30 min). – System **10**/DHA: SE 54, 25 m, temperature program: 80°C (10 min) – 10°C/min – 250°C (30 min). – System **12**/DHA: a) DB 23, 30 m + SE 54, 10 m, temperature program: 60°C (7 min) – 10°C/min – 245°C (15 min). – b) DB 1, 25 m, temperature program: 45°C (5 min) – 10°C/min – 250°C (20 min).

Materials: 1,3-Cyclohexadiene (**4**; Janssen 97%), 1,3-cycloheptadiene (**10**; Fluka, 98%), cycloheptatriene (**12**; Merck, 97%), [D_1]ethanol (Janssen, 99.6%), and D_2O (Deutero GMBH, 99.9%) were commerically available and used without further purification. – Diphenyl ether was purchased from Aldrich (99%) and thoroughly degassed with argon (99.998%). – 9,10-Dihydroanthracene (DHA; Janssen) and xanthene (**19**; Aldrich) were purified by repeated recrystallization from ethanol to ≥99% purity. 9,9′10,10′-D_4-9,10-Dihydroanthracene ([D_4]DHA) was prepared as described in ref.[12].

EPR: A solution of **4** (0.08 M) and xanthene **19** (1.00 M) in diphenyl ether was degassed by several "freeze-pump-thaw"[1] cycles and sealed in an EPR sample tube (diameter: 2 mm, glass thickness: 1.0 mm) by melting. It was transferred into the cavity of the EPR spectrometer and heated to 270 °C under the following conditions: Center field: 3327 gauss; sweep width: 60 gauss; modulation: 0.4; signal amplification: $2.0 \cdot 10^5$; microwave frequency: 9.330 GHz. The recorded spectrum is in good accordance with that recently published[2].

Thermolysis of 1,3-Cyclohexadiene (**4**) *with DHA in Diphenyl Ether:* A solution of 1,3-cyclohexadiene (**4**, 0.01 M), DHA (2.00 M) and *n*-nonane (0.01 M, internal standard) in diphenyl ether was distributed in 100-µl portions over 15 glass ampoules (inner diameter: 3 mm, glass thickness: 1 mm). They were thoroughly degassed by several freeze-pump-thaw cycles and sealed by melting under N_2. The ampoules were placed into a tin thermostat and heated constantly (±0.5 °C). At defined intervals they were taken out (the temperature of each sample was checked by a resistance thermometer PT-100) and cooled quickly. When all ampoules had been collected they were opened, transferred quantitatively to the sample containers of the autosampler and diluted with CH_2Cl_2 up to 1.0 ml. Finally, they were analyzed quantitatively by GC to follow the kinetics and by GC MS for product identification.

The kinetics was determined under pseudo-first-order conditions by using at least a 12-fold excess of the H donor. The rate constants k_2' were determined according to eq. (7). The rate constants k_2 were calculated from k_2' by correction for the thermal expansion using the thermal expansion coefficient for the solvent-DHA mixtures α_T[23] as indicated in eq. (7).

$$-\frac{\mathrm{d}\cdot[\mathbf{4}]}{\mathrm{d}t}\,k_{\mathrm{obs}}\cdot[\mathbf{4}] \tag{7}$$

where $k_{\mathrm{obs}} = k_2'[\mathrm{DHA}]$ and $k_2 = \alpha_T k_2'$.

Thermochemical Calculations: The reaction enthalpy ΔH_R of the rate determining step (retrodisproportionation) was calculated according to eq. (8)[24]:

$$\Delta H_R = \Delta H_f^0(g)\,[\mathbf{5}] + \Delta H_f^0(g)\,[\mathbf{6}] - \Delta H_f^0(g)\,[\mathbf{4}] - \Delta H_f^0(g)\,[\mathrm{DHA}] \tag{8}$$

The value for the standard enthalpy of formation $\Delta H_f^0(g)$ of the acceptor radical **5** was estimated by using eq. (9), where BDE(**7**) is the bond dissociation enthalpy of the allylic C−H bond in cyclohexene.

$$\mathrm{BDE}(\mathbf{7}) = \Delta H_f^0(g)\,[\mathbf{5}] + \Delta H_f^0(g)\,[\mathrm{H}^\bullet] - \Delta H_f^0(g)\,[\mathbf{7}] \tag{9}$$

BDE(**7**) is obtained from eq. (10),

$$\mathrm{BDE}(\mathbf{7}) = \mathrm{BDE}\,[\mathrm{H{-}CH(CH_3)_2}] + \mathrm{RSE} \tag{10}$$

where RSE is the radical stabilization enthalpy of the radical **5**.

Insertion of the corresponding thermochemical data[25] leads to the ΔH_R values of the systems **10**/DHA and **12**/DHA, respectively (see Table 1).

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