Tetrahedron Letters, Vol. 34, No. 48, pp. 7733-7736, 1993
Printed in Great Britain

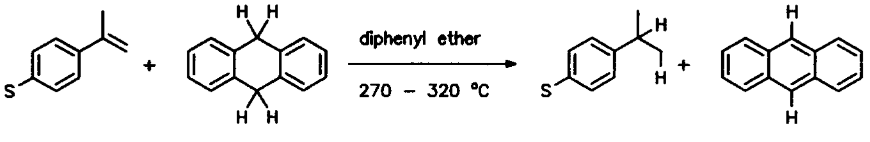
0040-4039/93 $6.00 + .00
Pergamon Press Ltd

Transfer Hydrogenation of p-Substituted α-Methylstyrenes by 9,10-Dihydroanthracene [1]

Matthias Gerst and Christoph Rüchardt *
Institut für Organische Chemie und Biochemie der Universität Freiburg, Albertstraße 21, D-79104 Freiburg, FRG

Summary: The rate constants k_2 of the uncatalyzed transfer hydrogenation of five p-substituted α-methylstyrenes **1a-e** vary less then a factor 2 (300 °C) which supports the proposed radical mechanism (scheme 2) and excludes hydride transfer as an alternative.

In previous work [1,2,3] it has been shown, that α-methylstyrene **1a** (S = H) is hydrogenated to cumene **3a** (S = H) by 9,10-dihydroanthracene (DHA) **2** at 270 - 320 °C without the addition of a catalyst.[4]

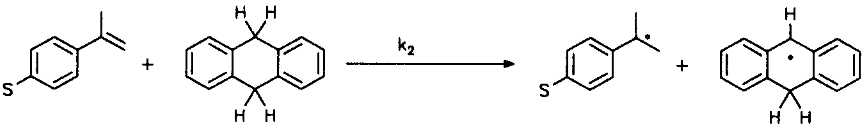


1 **2** **3** **4**

a S = H, **b** S = $C(CH_3)_3$, **c** S = Cl, **d** S = CN, **e** S = OCH_3

Scheme 1: Transfer hydrogenation of substituted α-methylstyrenes **1** by DHA **2**

Results from mechanistic investigations [2,3a] led to the conclusion that the reaction occurs in a three step process initiated by a rate determining molecule induced radical formation[5] between **1** and DHA **2**.



1 **2** **5** **6**

Scheme 2: Molecule induced radical formation by H-transfer

Experiments with 9,9',10,10'-tetradeuterio-9,10-dihydroanthracene proved that this step was irreversible under our reaction conditions.[2] The cumyl radicals **5** are rapidly trapped by excess DHA **2** and the 9-hydroanthyl radicals **6** disproportionate to DHA **2** and anthracene **4**.[6]

In order to get additional evidence for this mechanistic proposal and in particular for excluding a hydride transfer mechanism as an alternative[7] we investigated the influence of p-substituents S in α-methylstyrene on the reaction rate at different temperatures (270 - 320 °C). Substituent effects in radical reactions which are not subject to polar effects generally are small.[8]

The substituted α-metylstyrenes **1b** - **1e** were synthesized from the corresponding acetophenones by the Wittig reaction for **1b-d** or CH_3Li addition followed by dehydratisation for **1e**. The products were pure according to GC (> 99%). To determine the rate constants k_2, the ampoule technique[3a] and GC-analyses were used. The cumenes **3** and anthracene **4** were the only reaction products and found in yields >95 %. In table 1 the rate constants k_2 are summarized.

Table 1: Rate constants k_2 for the transfer hydrogenation of **1** by DHA **2**

T [°C][a]	10^5k_2 S = H	10^5k_2 S = $C(CH_3)_3$	10^5k_2 S = Cl	10^5k_2 S = CN	10^5k_2 S = OCH_3
270.0	3.88 ± 0.24	3.53 ± 0.17	4.29 ± 0.15	-	3.57 ± 0.04
280.0	5.22 ± 0.07	5.48 ± 0.24	7.45 ± 0.24	15.52 ± 0.60[b]	4.87 ± 0.48
290.0	7.82 ± 0.40	-	-	24.79 ± 0.37[c]	-
300.0	15.42 ± 0.31	15.43 ± 0.24	21.12 ± 0.21	36.66 ± 0.44[d]	17.02 ± 0.20
311.0	22.22 ± 0.55	25.29 ± 0.77	32.45 ± 0.44	-	26.47 ± 0.13
320.0	37.85 ± 0.31	43.03 ± 1.55	48.99 ± 1.66	96.04 ± 4.08	38.28 ± 0.30

Concentrations: **1** [0.08 M], **2** [1.0 M] in diphenyl ether; [a] T ± 0.5 °C; [b] T = 278.0 °C; [c] T = 288.0 °C; [d] T = 297.0 °C.

The minimal influence of the substituents S on the rates indicates that the conjugation energy between S and the double bond in **1** must be about the same as between S and the odd electron in **5**. Only for S = CN the rate is somewhat enhanced which is due to the large radical stabilization effect of CN substituents.[9]

From the temperature dependence of the rate constants k_2 the activation parameters were calculated by the Eyring equation (table 2).

Table 2: Activation parameters for the transfer hydrogenation of **1** by DHA **2**

Styrene derivative	$\Delta H^{\ddagger}$ [kcal mol^{-1}]	$\Delta S^{\ddagger}$ [e.u.]	$\Delta G^{\ddagger}_{300°C}$ [kcal mol^{-1}]
1a[10]	31.00 ± 1.32	-23.24 ± 2.29	44.32 ± 1.32
1b	30.76 ± 1.00	-23.54 ± 1.75	44.26 ± 0.98
1c	29.43 ± 0.93	-25.33 ± 1.63	43.94 ± 0.90
1d	27.07 ± 0.31	-28.01 ± 0.55	43.12 ± 0.38
1e	29.46 ± 0.62	-25.76 ± 1.09	44.23 ± 0.61

They are also nearly insensitive towards p-substituents as expected. The activation enthalpy $\Delta H^{\ddagger}$ for the reaction of α-methylstyrene **1a** was calculated from thermochemical data as $\Delta H^{0}(f,g) = 31.5 \pm 2.0 - 34.2 \pm 2.3$ kcal mol^{-1} [2] assuming radical intermediates. This supports the proposed mechanism. The activation entropies $\Delta S^{\ddagger}$ for this bimolecular reaction are negative as expected and decrease parallel with $\Delta H^{\ddagger}$. Therefor $\Delta G^{\ddagger}_{300°C}$ was almost constant in the series **1a** - **1e**. A compensation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ was also observed in other uncatalyzed transfer hydrogenations.[11] It proved to be significant for the reaction mechanism and not due to error compensation.[12]

The kinetic results of the transfer hydrogenation of p-substituted α-methylstyrenes **1** by DHA **2** are in accord with the proposed radical mechanism and exclude hydride transfer as an alternative.

Acknowledgements:

The authors are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

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(Received in Germany 16 August 1993; accepted 29 September 1993)