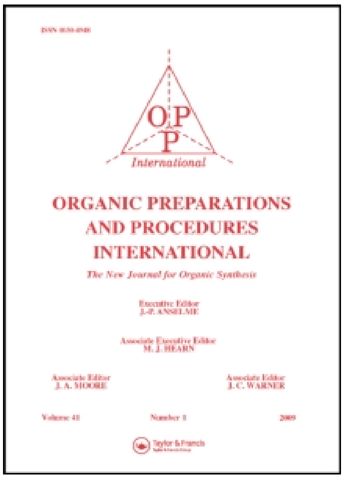

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DIIMIDE REDUCTION OF SUBSTITUTED STYRENES AND OF PHENYL-1,3-BUTADIENES

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DIIMIDE REDUCTION OF SUBSTITUTED STYRENES AND OF PHENYL-1,3-BUTADIENES

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We have studied the synthetic utility of the diimide reductions[1,2] of styrene derivatives (IIa-k) and phenyl-1,3-butadienes. The relative rates of these reductions were also investigated since they relate to the practicability of the procedure. The results are given in Table 1. Similar treatment of styrenes substituted on the side-chains (IIIa-c) gave the corresponding reduced compounds (Table). Interestingly, the reduction of

$$\underset{\text{I}}{KO_2CN{=}NCO_2K} + \underset{\text{II}}{XC_6H_4CH{=}CH_2} \longrightarrow XC_6H_4CH_2CH_3 \qquad (1)$$

a) X = H b) X = 4-CH_3 c) X = 3-CH_3 d) X = 2-CH_3 e) X = 4-*t*-Bu

f) X = 4-OCH_3 g) X = 3-OCH_3 h) X = 4-Cl i) X = 3-Cl j) X = 4-Br

k) X = 4-NO_2

$$I + \underset{III}{C_6H_5CX{=}CHY} \longrightarrow \underset{IV}{C_6H_5CHXCH_2Y} \qquad (2)$$

a) $X = CH_3$, $Y = H$ b) $X = H$, $Y =$ trans-CH_3 c) $X = Ph$, $Y = H$

cis- and trans-stilbenes were not satisfactory under the same conditions, suggesting sensitivity to steric hindrance. Competitive reductions of the alkenes were carried out using styrene (IIa) as the standard, and the products were analyzed by GLC. Relative reactivities (Table) were calculated from the expressions previously reported by Garbisch et al.[2]

TABLE 1. Yield and Relative Rates of Diimide Reduction of Styrenes (II) and Butadienes (III)[a]

Cmpd	Yield (%)	k/ks[b]	bp/torr	lit. bp	Bielstein Ref.
IIa	98[c]	1.00	57-58/50	56.7/48	5, III 780
IIb	98	1.12	68-59/30	45.7/10	5, III 896
IIc	98	1.07	67-68/30	45.7/10	5, III 894
IId	99	0.92	68-69/30	48.5/10	5, III 891
IIe	96	1.10	98-100/15	102.105/17	5, III 1024
IIf	99	1.05	82-84/15	83-84/16	6, III 1665
IIg	98	1.10	83-84/15	75-76/12	6, III 1662
IIh	98	0.76	75-77/20	109/75.9	5, III 788
IIi	98	0.82	75-78/20	65-68/13	5, III 787
IIj	96	0.79	94-95/20	95-96/20	5, III 796
IIk	98	0.88	90-92/1	93-94/2	5, III 803
IIIa	99	0.052	63-64/30	38.3/10	5, III 879
IIIb	99	0.039	65-66/30	43-44/10	5, III 867
IIIc	99	0.023	130-132/10	131-132/11	5, III 1825

a) All reductions were carried out at 0° and the yields were determined by GLC using ethylbenzene as internal standard. b) All values are ± 0.03 or less. c) 4-Ethyltoluene used as internal standard.

The reduction of trans-1-phenyl-1,3-butadiene with diimide gave only trans-1-phenyl-1-butene in a good yield while similar treatment of 2-phenyl-1,3-butadiene gave 2-phenyl-1-butene as the major product (85%), 3-phenyl-1-butene being formed in 15% yield. On the other hand, it is well known that in the catalytic hydrogenation of dienes, 1,2- and 1,4-addition of hydrogen and isomerization take place concurrently to give a mixture of several products.[3] Neither 1,4-addition of hydrogen nor isomerization of the products was observed in the present reduction of dienes with diimide.

EXPERIMENTAL SECTION

Boiling points are uncorrected. The GLC analyses were performed on a Yanako GCG-550T with a Silicone DC 550 (25%)-Celite 545 (2 m) column. 1,1-Diphenylethylene (IIIc) and phenyl-1,3-butadienes were prepared by dehydration of the corresponding alcohols.[4] I was prepared by the known procedure.[5] All the other compounds were commercially available and were distilled before use.

Diimide Reduction. General Procedure.- To a suspension of potassium azodicarboxylate (I) (3.88 g, 20 mmol) in 25 ml of methanol containing the alkene (10 mmol) was added a solution of acetic acid (2.4 g, 40 mmol) in 15 ml of methanol at 0° over 30 min with stirring. The reaction mixture was stirred for an additional hr, then neutralized with aq. Na_2CO_3 and extracted with ether. The ethereal extract was dried over Na_2SO_4. After removal of the ether, the product was purified by distillation and identified by comparison of its GLC retention time with that of the authentic sample.[6]

The reduction of trans-1-phenyl-1,3-butadiene with diimide gave trans-1-phenyl-1-butene (97% yield by GLC analysis), bp. 88-89°/15 mm, lit.[7] bp. 200°/760 mm. The GLC retention time of the product was identical with that of the authentic sample prepared by the known procedure.[7] The reduction of 2-phenyl-1,3-butadiene with diimide gave a mixture of 2-phenyl-1-butene (85%) and 3-phenyl-1-butene (15%) as determined by GLC. The total yield determined by GLC was 95%. Although the two isomers could not be separated by fractional distillation, the GLC retention times agreed with those of authentic samples.[7,8]

Competitive Reduction.- To a mixture of I (0.97 g, 5 mmol), each alkene (IIb-k, 5 mmol), and IIa (5 mmol) in 10 ml of methanol was added a solution of acetic acid (0.6 g, 10 mmol) in 10 ml of methanol at 0° with stirring. In the cases of IIIa-c, competitive reductions were carried out with I (5 mmol), each alkene (20 mmol), and IIa (5 mmol). After the usual work-up, the ethereal extract was subjected to GLC. The relative rates were determined by the peak areas of GLC with the use of response factors. In general, two or more runs were made on each alkene and the average values are given in the Table.

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