

## Selectivity in Di-imide Reductions of Aldehydes, Ketones, and Hetero-substituted Olefins

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PAST investigations<sup>1</sup> have established di-imide ( $H_2N_2$ ) as an unstable specie characterized by unusual and selective reducing action on organic substrates. In this contribution we reveal yet other novel and useful modes of hydrogenation, associated with the conversion of aldehydes and ketones into the corresponding alcohols, and the behaviour toward olefins substituted in the proximity of the double bond by halogen, nitrogen, and oxygen functions.

As demonstrated in Table 1, the reduction to alcohols of purely aliphatic aldehydes and ketones by di-imide (generated from disodium azodicarboxylate by the action of acetic acid) proceeded under standardized conditions in poor yields, ranging from essentially zero in the cases of  $\alpha\beta$ -unsaturated ketones to 14% with acetone. By contrast, yields of alcohols in the aromatic series

TABLE 1. Reduction of aldehydes and ketones\*

Aldehyde or ketone	Product	Yield (%) <sup>b</sup>
PhCHO	PhCH <sub>2</sub> ·OH	56
PhCOMe	(±)-PhCHMe·OH	31
Ph <sub>2</sub> CO	Ph <sub>2</sub> CH·OH	26
Me <sub>2</sub> CO <sup>a</sup>	Me <sub>2</sub> CH·OH	14
Et <sub>2</sub> CO	Et <sub>2</sub> CH·OH	6·5
[CH <sub>2</sub> ] <sub>5</sub> >CO	[CH <sub>2</sub> ] <sub>5</sub> >CH·OH	9·3
Me·[CH <sub>2</sub> ] <sub>5</sub> ·CHO	Me·[CH <sub>2</sub> ] <sub>5</sub> ·CH <sub>2</sub> ·OH	1·0
Me <sub>2</sub> C=CH·COMe	Me <sub>2</sub> CH·CH <sub>2</sub> ·COMe	3·5
	(Alcohol)	0·0
Cyclohex-2-enone	[CH <sub>2</sub> ] <sub>5</sub> >CO	6·0
	(Alcohol)	0·0

\* Reductions were carried out by addition of two moles of acetic acid in methanol to equimolar amounts of carbonyl compound and disodium azodicarboxylate, both dissolved in methanol

<sup>a</sup> 2-Ethoxyethanol as solvent

<sup>b</sup> Yields determined by v.p.c. methods

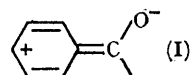
<sup>1</sup> For a recent compilation of references, see the review of F. Aylward, *Chem. and Ind.*, 1962, 484.

under parallel conditions were sensibly greater, as high as 56% in the case of benzaldehyde. Although display examples were not sought, it is evident that di-imide could be useful for the preferential reduction of aromatic aldehyde and ketone functions—despite the steric encumbrance—in the presence of their aliphatic counterparts.

In a similar vein, the saturation of the olefinic bonds by di-imide in representative allyl systems (alcohol, bromide, ether, and amine) proceeded in satisfactory yields (50–99%) and without hydrogenolysis. On the other hand, reduction of double bonds in various vinyl cases (bromide, ether, and amine) were considerably slower under similar conditions, with large proportions of starting material being untouched in most cases. Again, the synthetic utility is obvious. In this series, as in the ketone–aldehyde study, no attempt was made to realize optimum yields; but rather, emphasis was placed on comparative behaviour under arbitrary but standardized conditions. Since di-imide by itself can suffer oxidation–reduction to nitrogen and hydrazine, the yields of reduction products roughly represent comparative rates of reduction.

Mechanistically, these results are embraced by the heuristic principle already expressed,<sup>2</sup> namely that di-imide reductions of electrically symmetrical multiple bonds proceed more rapidly than reduction of more polar functions. Although reductions of allylic and simple olefinic bonds proceed as a general rule without difficulty, saturation of vinyl halide, ether, and amine is considerably slower because of the simple electron-withdrawing effect

of the hetero-atom on the carbon to which it is attached. Similarly, attack on (more polar) aliphatic aldehyde and ketone carbonyl groups is sluggish; whereas the resonance contribution (*e.g.* I) which decreases positive charge on the aromatic carbonyl carbon (and thereby with



nucleophilic agents leads to a slower rate of reaction) permits a more rapid interaction with the di-imide agent.

TABLE 2. Reduction of hetero-substituted olefins\*

Olefin	Proton source	Yield of saturated product
CH <sub>2</sub> =CH·CH <sub>2</sub> ·OH	octanoic acid	99
CH <sub>2</sub> =CH·CH <sub>2</sub> ·Br	water	62
CH <sub>2</sub> =CH·CH <sub>2</sub> ·OPh	acetic acid	87
CH <sub>2</sub> =CH·CH <sub>2</sub> ·NHPh	acetic acid	50 <sup>a</sup>
MeCH=CHBr	water	~0
CH <sub>2</sub> =CH·OBu <sup>a</sup>	acetic acid	10–15
Dihydro-4H-pyran	acetic acid	~0
Dihydro-1,4-dioxin	acetic acid	~0
1-Cyclohex-1'-enyl-pyrrolidine	acetic acid	~0

\* Reductions were carried out in methanol with two moles of dipotassium azodicarboxylate, and yields were based on v.p.c. determinations.

<sup>a</sup> Decomposition of product on v.p.c. was noted.

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<sup>2</sup> E. E. van Tamelen, R. S. Dewey, M. F. Lease, and W. H. Pirkle, *J. Amer. Chem. Soc.*, 1961, **83**, 4302.