69%; and *cis*-3-hexene, 5%. The calculated populations of butadiene conformers from these data are 93% *s-trans* and 7% *s-cis*.

Both determinations of the compounds produced on adding methyl radicals to butadiene are in agreement with the calculations of Aston and Szasz[3] and strongly support the concept that we are dealing with allylic radicals with short lifetimes as intermediates in each case. The chemical evidence indicates that *s-cis*-butadiene is present in 3–7% under the conditions studied here.

[8] Robert A. Welch Visiting Scientist, 1960–1961.

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SELECTIVITY AND MECHANISM OF DIIMIDE REDUCTIONS

Sir:

Previous reports from this and other Laboratories[1a–d] have dealt with the detection and utilization of the unstable inorganic species H_2N_2 (diimide, diazene), generated by, *e.g.*, oxidation of hydrazine,[1b,c] decarboxylation of azodicarboxylic acid[1b,c] and thermal decomposition of *p*-toluenesulfonylhydrazine.[1d] We now present results which demonstrate the striking selectivity of diimide as a reducing agent, which property leads to a fuller appreciation of the character of the reduction mechanism.

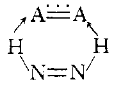
Under conditions where representative carbon–carbon double bonds are reduced readily (1–2 moles of azodicarboxylic acid in solvent at room temperature), these substances, *e.g.*, are substantially if not completely unattacked: acetonitrile, benzonitrile, nitroethane, nitrobenzene,[2] benzalaniline,[3] benzyl sulfide, dimethyl sulfoxide, dibenzyl sulfoxide, benzyl disulfide and the ethylene dithioketal of cyclohexanone.[4] In addition, indications are that carbonyl compounds are reduced with difficulty by diimide, in that carboxylic acid, γ-lactone[5] and ketone (cyclohexanone) functions are seemingly untouched.[6,7]

The above results suggested an exemplary reduction which would demonstrate the high order of selectivity realizable by means of diimide, namely, saturation of the double bonds in allyl disulfide without disruption of the disulfide link, which change can be brought about directly in no other way, as far as we are aware. In the most

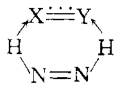
$$(CH_2{=}CH{-}CH_2S)_2 \longrightarrow (CH_3CH_2CH_2S)_2$$

successful experiments, allyl disulfide was treated with 3 equivalents of acetic acid, or with 3 moles of tosylhydrazine in ethylene glycol (heating); conversion to propyl disulfide fell in the range 93-100% (v.p.c.).

Findings accumulated thus far suggest that *diimide reductions of symmetrical multiple bonds* ($C{=}C$, $C{\equiv}C$, $N{=}N$, $O{=}O$) *proceed readily*,[8] *whereas reductions of more polar functions* ($C{\equiv}N$, $O{\leftarrow}N{=}O$, $C{=}N$, $S{=}O$, $S{-}S$, $S{-}C{-}S$, $C{=}O$) *are more difficult.* This generalization may be expressed in terms of an energetically favorable, symmetrical (A equals A) and largely uncharged transition state (I) for diimide reductions, involving simultaneous transfer of neutral hydrogen to substrate; and a less likely transition-state type (II) in which X and Y represent different atoms, each of which bears therefore a partial charge.[9]



I



II

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RECEIVED SEPTEMBER 16, 1961

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[1] (a) S. G. Cohen, R. Zand and C. Steel, *J. Am. Chem. Soc.*, **83**, 2895 (1961); (b) E. J. Corey, D. J. Pasto and W. L. Mock, *ibid.*, **83**, 2957 (1961); (c) E. E. van Tamelen, R. S. Dewey, and R. J. Timmons, *ibid.*, **83**, 3725 (1961); (d) R. S. Dewey and E. E. van Tamelen, *ibid.*, **83**, 3729 (1961).

[2] It is worthy of note that aromatic nitro compounds can be reduced in good yield to anilines by means of hydrazine in the presence of a metal hydrogenation catalyst at room temperature (A. Furst and R. E. Moore, *ibid.*, **79**, 5492 (1957). In these cases it would appear that diimide is not involved.

[3] Stilbene and azobenzene are reduced easily by H_2N_2.

[4] V. Georgian, R. Harrison and N. Gubisch, *ibid.*, **81**, 5834 (1959), have reported that dithioketals can be reductively desulfurized by means of hydrazine, best in the presence of alkali, under more drastic conditions.

[5] See the case of gibberellic acid, B. E. Cross, *J. Chem. Soc.*, 3022 (1960).

[6] However, in the single aldehyde case studied (benzaldehyde), reduction to the alcohol occurred.

[7] It is possible that under conditions more stringent than specified above, reduction of the functional groups listed might be realized.

[8] Reduction rates of olefins and acetylenes must be comparable, as shown by isolation of starting acetylene, *cis* olefin and alkane after controlled reduction of diphenylacetylene[1b] and hexine-2 (unpublished results secured in this Laboratory by R. J. Timmons).

[9] As pointed out before,[1b,d] the form $N^-{=}N^+H_2$ must also be considered for the structure of "diimide."

[10] National Institutes of Health Postdoctoral Fellow.

[11] National Science Foundation Fellow (summer 1961).