

ever, if, for example, the bands at 445 and at 478 cm^{-1} were used for the measurements with the KBr optics, the results obtained by use of the peak intensities in the carbon disulfide and the *n*-heptane solution did not agree with the previous one, although results obtained by the area intensities agreed very well. This can be seen from Table III.

Although Allinger, *et al.*, used peak intensities in their estimation of the energy difference, it is not always safe to use peak intensities instead of area intensities. According to our measurements the results obtained by peak intensities cannot be correct, especially when the bands used are lying in the region where the absorption of prisms becomes noticeable. Further evidence for this is given in Table IV.

TABLE IV
ENERGY DIFFERENCE DETERMINED BY USE OF THE DIFFERENT PRISMS

Temp.	ν_{max}	Form	$\ln(T_0/T)_{\nu_{\text{max}}}$	$\Delta\nu_{1/2}^a$	K	$C_n A_n / C_s A_s$	Ratio of peak intensities
(1) CS_2 solution (0.090 mole/l.); prism, NaCl; spectral slit-width, $S = 2.54 \text{ cm}^{-1}$ at 699 cm^{-1} , $S = 2.65 \text{ cm}^{-1}$ at 714 cm^{-1}							
22°	699	a	1.36	9.8	1.56	2.6	3.7
	714	e	0.368	14.0	1.55		
-24°	699	a	1.45	8.3	1.56	2.1	3.4
	714	e	0.424	14.0	1.55		
ΔE (by area intensity)			0.75 kcal./mole (stable form, e)				
ΔE (by peak intensity)			0.26 kcal./mole				
(2) CS_2 solution (0.090 mole/l.); prism, KBr, spectral slit-width, $S = 2.87 \text{ cm}^{-1}$ at 699 cm^{-1} ; $S = 2.96 \text{ cm}^{-1}$ at 714 cm^{-1}							
24°	699	a	1.17	9.7	1.56	3.6	3.6
	714	e	0.322	10.0	1.53		
-24°	699	a	1.42	8.9	1.56	2.8	2.8
	714	e	0.507	9.0	1.53		
ΔE (by area intensity)			0.78 kcal./mole (stable form, e)				
ΔE (by peak intensity)			0.78 kcal./mole				

It should be noted that the results obtained by area intensities are nearly constant throughout these measurements in good agreement with our previous results.¹

From the dependence of the intensities on temperature it became clear that both of the bands at 535 and 541 cm^{-1} are due to the same *e*-isomer. Thus one of the assignments of our previous article should be corrected.

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TWO CHEMICAL DETERMINATIONS OF THE POPULATION OF CONFORMATIONS IN 1,3-BUTADIENE

Sir:

For many years it has been generally accepted that at room temperature 1,3-butadiene exists primarily in the *s-trans* form. This contention has been supported by a variety of physical evidence.^{1,2}

(1) D. Craig, J. J. Shipman, and R. B. Fowler, *J. Am. Chem. Soc.*, **83**, 2885 (1961).

(2) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 3rd ed., 1960, pp. 290-292.

On the basis of thermodynamic data Aston and Szasz³ concluded that the *s-cis* form made up 4% of the whole. As late as 1959, Pauling² could state that no chemical evidence relating the amounts of the two forms had appeared. We wish now to present such data.

The basis for the determinations reported here is the observation by Walling, *et al.*,⁴ that the free radical chlorination of *cis* or *trans* 2-butene produced only the respective *cis*- or *trans*-1-chloro-2-butenes. This result was interpreted as meaning that the short-lived allylic free radicals, produced during the chlorination reaction, were capable of maintaining their original geometry. If this is so, then it is evident that an examination of the 1,4-addition products formed by radical attack on butadiene may offer a direct measurement of the amounts of *s-trans*- and *s-cis*-butadiene present in the reaction mixture. It should be pointed out, however, that in the slower chain propagating step of the radical polymerization of butadiene the ratio of *cis* to *trans* double bonds in the product varies considerably with temperature.⁵ Thus, the use of this method for determining the population of conformations in 1,3-butadiene will be most reliable in cases where the life time of any intermediate allylic radicals is comparatively short.

The electrolysis of potassium acetate in methanol-butadiene mixtures has been shown previously to lead to 3-methyl-1-pentene and *trans*-3-hexene among other products.⁶ In the original studies no *cis*-3-hexene was observed and an argument was advanced postulating a heterogeneous reaction involving absorbed radicals. We now find that by using a fifty-foot column of 23% dimethylsulfolane on Chromosorb at room temperature it is possible to demonstrate the presence of *cis*-3-hexene in the reaction product by vapor phase chromatography. The hexene fraction from the Kolbe electrolysis gave the analysis: 3-methyl-1-pentene, 21% *trans*-3-hexene, 77%; and *cis*-3-hexene, 2%. Their results indicate that *ca.* 97% of the butadiene exists in the *s-trans* form while *ca.* 3% is in the *s-cis* form. The close agreement between the experimental observation and the predicted values³ suggests strongly that no special effects need be evoked to explain the products from the Kolbe electrolysis, and that we are actually measuring the population of butadiene conformers.

Kharasch, Holton, and Nudenberg⁷ have reported that the treatment of methyl iodide with magnesium in the presence of isoprene does not yield any 1,2- or 1,4-addition products of methyl radicals to the isoprene in contrast to the results with other alkyl halides. However, we find that when methyl iodide and magnesium react in the presence of butadiene a small yield of hexenes is formed. The analysis of this mixture gave the results: 3-methyl-1-pentene, 26%; *trans*-3-hexene,

(3) J. G. Aston and G. Szasz, *J. Chem. Phys.*, **14**, 67 (1946).

(4) C. Walling, B. B. Jacknow, and W. Thaler, Abstracts, 136th National Meeting, American Chemical Society, Atlantic City, N. J.

(5) C. Walling, "Free Radicals in Solution," John Wiley and Sons, New York, N. Y., 1957, p. 230.

(6) W. B. Smith and H.-G. Gilde, *J. Am. Chem. Soc.*, **81**, 5325 (1959), and **83**, 1355 (1961).

(7) M. S. Kharasch, P. G. Holton, and W. Nudenberg, *J. Org. Chem.*, **19**, 1600 (1954).

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 Szasz³ 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 H₂N₂ (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 benzaldehyde,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

(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).

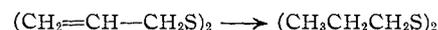
(2) It is worthy of note that aromatic nitro compounds can be reduced in good yield to anilines by means of hydrazine in the presence of a metal hydrogenation catalyst at room temperature (A. Furst and R. E. Moore, *ibid.*, **79**, 5492 (1957). In these cases it would appear that diimide is not involved.

(3) Stilbene and azobenzene are reduced easily by H₂N₂.

(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.

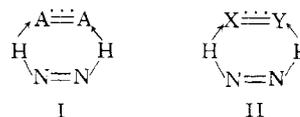
difficulty by diimide, in that carboxylic acid, γ -lactone⁵ and ketone (cyclohexanone) functions are seemingly untouched.^{6,7}

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



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=C=N, 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 sub-



strate; 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

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(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 hexene-2 (unpublished results secured in this Laboratory by R. J. Timmons).

(9) As pointed out before,^{1b,d} the form N \equiv N⁺H₂ must also be considered for the structure of "diimide."

(10) National Institutes of Health Postdoctoral Fellow.

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