

Another sample of IVa (0.13 g., 0.68 millimole) was hydrolyzed with 25 ml. of 0.12 *N* ethanolic potassium hydroxide (0.003 mole) and the nitrogen collected in a manner similar to that already described. The corrected volume of nitrogen amounted to 16.8 ml. or to 97% (17.3 ml., 0.68 millimole) of the theoretical value.

Uncoupling of 1,6-Bis-(*p*-chlorophenyl)-3,4-diacetyl-1,5-hexazadiene (Ia) with Concentrated Sulfuric Acid.—To 5.0 ml. of cold concentrated sulfuric acid was added portionwise 0.5 g. of 1,6-bis-(*p*-chlorophenyl)-3,4-diacetyl-1,5-hexazadiene (Ia) (0.0013 mole). When all the solid had dissolved, the sulfuric acid solution was poured on 50 g. of cracked ice. The resulting solution was added to a cold alkaline solution of 2-naphthol. A deep red precipitate was deposited which was collected, washed with water and dried in a vacuum desiccator. Recrystallization from ethanol gave 0.64 g. (97% yield) of 4'-chlorobenzeneazo-2-naphthol, m.p. 158–159° (lit.¹² 158–159°).

Degradation of Ia with Ethanol.—To a three-necked round-bottomed flask equipped with a reflux condenser, a gas inlet tube and containing 500 ml. of absolute ethanol, was added 23.6 g. (0.06 mole) of Ia. Two traps containing an acidified aqueous ethanol solution of 2,4-dinitrophenylhydrazine (0.07 mole) were connected in series and attached by means of a short piece of rubber tubing to the top of the

reflux condenser. The mixture was warmed slowly, the liberation of nitrogen being evident almost immediately with simultaneous hydrazone formation occurring in the first trap. After the evolution of gas had subsided, a slow stream of nitrogen was passed into the flask while the reaction mixture was maintained under gentle reflux (40 minutes).

The reflux condenser was detached and the solvent removed by distillation, the distillate being caught in one of the traps. The hydrazone was collected, recrystallized from ethanol and amounted to 26.9 g. (82% of theoretical amount), m.p. 146–147° alone and when mixed with an authentic sample of acetaldehyde 2,4-dinitrophenylhydrazone.

The tarry residue remaining in the still-pot yielded, on steam distillation, a few drops of a yellow oil and 0.1 g. of a white solid, m.p. 300°. Neither of these products was identified.

The clear aqueous solution remaining in the distillation flask was decanted from the tarry insoluble material and evaporated to dryness. The white residue was dissolved in 30 ml. of ethanol, treated with Norit and diluted to a volume of 180 ml. with absolute ether. The white solid which deposited was collected (weight 6.0 g., 95% yield) and identified from mixed melting points (137–139°) as 1,2-diacetylhydrazine.

(12) K. J. P. Orton and R. W. Everatt, *J. Chem. Soc.*, **93**, 1020 (1908).

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY]

Configuration of Free-Radicals. Non-stereospecificity of *cis*- and *trans*-2-Butene-Sulfur Dioxide Copolymerizations

BY PHILIP S. SKELL, ROBERT C. WOODWORTH¹ AND JAMES H. MCNAMARA²

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Evidence is presented that demonstrates the copolymerization of *cis*- and *trans*-2-butene with sulfur dioxide is not stereospecific.

Introduction

A pyramidal structure for free radicals is indicated by two experiments in the 1-bicyclo-[2,2,1]heptyl system. Kharasch, Engelmann and Urry³ found that the decomposition of the peroxide of 1-apocamphanecarboxylic acid in carbon tetrachloride produced 1-chloroapocamphane, and Blickenstaff and Hass⁴ found that the nitro products from the high temperature nitration of bicyclo-[2,2,1]heptane were 50% 1-nitro compound.

A considerable body of evidence⁵ has accumulated relative to the stereochemistry of free radicals which are not constrained to a rigid pyramidal configuration by a bicyclic system. Omitting from this discussion all consideration of radicals in which resonance requirements demand a planar configuration, the conclusion that follows from the main body of evidence is that non-bicyclic free

radicals are either planar or, if they are pyramidal, inversion takes place more rapidly than any reaction which converts the radical center to a stable tetravalent atom. For example, the 3-trichloro-

$$\begin{array}{c} \text{CCl}_3 \\ | \\ \text{methyl-2-butyl radical, } \text{CH}_3\text{CH}-\dot{\text{C}}\text{HCH}_3, \end{array}$$

suffers complete equilibration among all rotational conformations of both diastereomeric forms more rapidly than the radical reacts with bromotrichloromethane.

Stereospecificity in Radical Reactions

A critical examination of the exceptions to the generalizations stated above is the main object of this paper.

One of us (P.S.S., 1947⁶) observed that the reaction of ethyl (–)- α -bromopropionate ($\alpha_D -3.78^\circ$, neat, 1 dcm.) with 1-butene in the presence of small amounts of acetyl peroxide⁶ produced ethyl α -methyl- γ -bromocaproate ($\alpha_D -0.07^\circ$, neat 0.25 dcm.). In view of the experimental results reported in the present paper, the slight activity observed in the product is better explained by asymmetric induction than by a stable enantiomorph of the free radical.

(6) These experiments are mentioned here because references to this unpublished work have appeared in the literature. For details regarding this type of preparation see, M. S. Kharasch, P. S. Skell and P. Fisher, *THIS JOURNAL*, **70**, 1055 (1948).

(1) National Science Foundation Fellow.

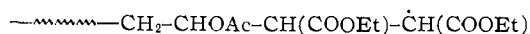
(2) In partial fulfillment of the requirements for the Ph.D. Thesis, Pennsylvania State University, 1956.

(3) M. S. Kharasch, F. Engelmann and W. H. Urry, *THIS JOURNAL*, **65**, 2428 (1943).

(4) R. T. Blickenstaff and H. B. Hass, *ibid.*, **68**, 1431 (1946).

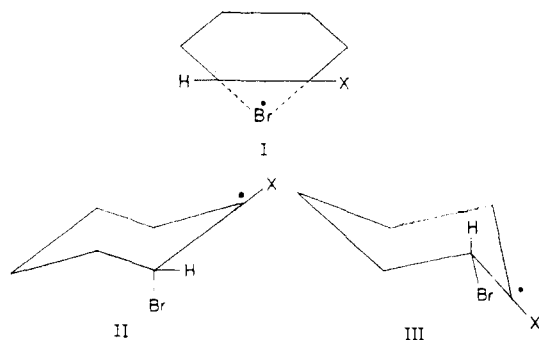
(5) For references to much of the pertinent literature, see: (a) P. S. Skell and R. C. Woodworth, *ibid.*, **77**, 4638 (1955), (b) G. A. Russell, *ibid.*, **78**, 1038 (1956), (c) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 443, and (d) R. L. Shriner, R. Adams and C. S. Marvel, "Organic Chemistry (Gilman)," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 383.

Tong and Kenyon⁷ reported that the heats of formation (from heats of polymerization and isomerization) of the 1:1 copolymers vinyl acetate-diethyl maleate and vinyl acetate-diethyl fumarate differed by 0.7 kcal./mole, an amount which was considered to be just outside the standard deviations. This small difference in ΔH_f was explained in terms of diastereomeric copolymers and consequently is suggestive of reactive chain ends which are stable diastereomeric radicals.



Dainton and co-workers⁸ reported that the heats of copolymerization of *cis*- and *trans*-2-butene with SO₂ differed by 0.8 kcal./mole. With the aid of the known heat of isomerization of the olefins, the difference in heats of formation of the copolymers was calculated to be 2.33 ± 0.6 kcal./mole (*cis* minus *trans*). Analysis of the kinetic data indicated that chain growth involved successive additions of 2-butene and SO₂ units rather than addition of a 2-butene-SO₂ complex to the reactive end of the chain.⁹ From this experimental basis it was concluded that a chain with a 2-butyl radical end, $\sim\sim\sim\sim\text{---SO}_2\text{---CH(CH}_3\text{)---}\dot{\text{C}}\text{HCH}_3$, reacts with SO₂ more rapidly than it is equilibrated among the diastereomeric radicals.¹⁰

Goering and co-workers¹¹ have studied the free radical additions of hydrogen bromide, hydrogen sulfide, thiophenol and thioacetic acid to 1-substituted cyclohexenes and found that the added fragments have a *trans* relationship. Since the two bulky substituents are in a *cis* relationship, these syntheses afford a new and elegant route to the thermodynamically less-stable isomers. The



initial interpretation of these results in terms of intermediate I has been modified to account for the isolation of some *cis* product in the addition of

(7) L. K. J. Tong and W. O. Kenyon, *THIS JOURNAL*, **71**, 1925 (1949).

(8) G. M. Bristow and F. S. Dainton, *Nature*, **172**, 804 (1953); *Proc. Roy. Soc. (London)*, **A229**, 509, 525 (1955).

(9) See also, C. Walling, *J. Polymer Sci.*, **16**, 315 (1955).

(10) Correspondence with Professor Dainton was initiated July, 1955. In recent communications from Professor Dainton (6/25/56 and 9/24/56) he has stated that all the new calorimetric data suggest the ΔH_f are identical. These results will appear in *Trans. Faraday Soc.* under the names F. S. Dainton, J. Diaper, K. J. Ivin and D. R. Sheard. However, proof that the ΔH_f of the copolymers are identical within the experimental error still leaves open the possibility that the copolymers are diastereoisomers.

(11) (a) H. L. Goering, P. I. Abell and B. F. Aycock, *THIS JOURNAL*, **74**, 3588 (1952); (b) H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955); (c) H. L. Goering, D. I. Relyea and D. W. Larsen, *ibid.*, **78**, 348 (1956). See also F. G. Bordwell and W. A. Hewett, Abstracts of papers presented at the 126th Meeting of the American Chemical Society, p. 6-O, September 13, 1954.

the sulfur compounds. The later evidence suggests that *cis* compounds are obtained in a kinetically controlled process and thus leads to the suggestion that II was produced initially and was subsequently isomerized in a slow step to III (II \rightarrow *cis* adduct and III \rightarrow *cis* and *trans* adduct). On the basis of this evidence one is led to the tentative conclusion that chair-chair interconversions in the cyclohexane system II may be slower than the reaction of this radical with HBr. However, in this type of complex system alternative interpretations are possible and consequently further experimentation is required.

2-Butene-SO₂ Copolymerization

Since one of the major obstacles to a uniform rationale in the field of radical stereochemistry stemmed from the Bristow and Dainton reports with references to the SO₂-2-butene copolymers, a two-pronged experimental approach, examination of these copolymers and determination of the relative rates of reaction was employed in an effort to resolve this situation.

Numerous samples of 2-butene-SO₂ copolymers were prepared from *cis*- and *trans*-2-butene employing a variety of conditions. In all cases reaction samples were paired so that the *cis*- and *trans*-2-butene samples were subjected to identical reaction conditions. The results from some of these experiments are summarized in Table I. Paired sets are indicated by the same arabic numeral designating the run. Initiation of the polymerization by benzoyl peroxide and light and inhibition by hydroquinone support the conclusions of Dainton and co-workers that the polymerization involves free radicals. Since the copolymers obtained by silver nitrate initiation appeared to be identical with the others, presumably this reagent also initiates a free radical polymerization. In most cases more product was obtained from the member of the pair that contained the *cis*-2-butene. This is consistent with the relative reactivities of these olefins for addition of $\cdot\text{CCl}_3$,^{5a} $k_{cis}/k_{trans} = 2.4$. In no instance was any isomerization of the unreacted olefin detectable, thus indicating, in agreement with Dainton and co-workers, that at 0 and -75° $k_{propagation}$ is much larger than $k_{depropagation}$.

Bristow and Dainton reported that Nujol mulls of the copolymers from *cis*- and *trans*-2-butene gave identical infrared spectra. All of the copolymers indicated in Table I were ground in KBr and compressed to transparent pellets for examination.¹² Although numerous sharp bands could be observed, there was not an appreciable difference in the spectra of these copolymers or those of samples of the "diastereomers" furnished by Professor Dainton. Since diastereomers usually show distinct spectral differences in the 10-15 μ region, this evidence strongly indicates the polymers are not diastereomers.

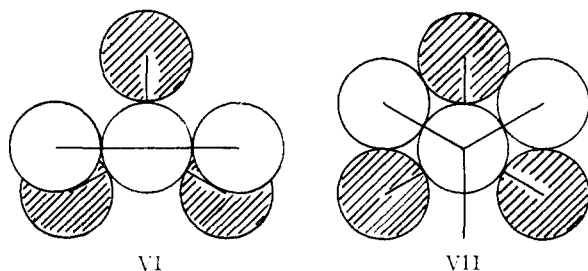
Since the possibility exists (though very unlikely) that the two diastereomeric polymers have indistinguishable infrared spectra, an alternative approach to the problem was sought. The pro-

(12) M. M. Simson and M. J. O'Donnell, *ibid.*, **74**, 1805 (1952).

possible to arrive at a lower limit¹⁶ of 1×10^{11} mole⁻¹ sec.⁻¹ for the absolute rate constant, k_3 . Since it is probable that the rates of rotations and inversions (k_{rac})¹⁷ are between 10^8 – 10^{13} sec.⁻¹, the value of $k_{rac}/(k_3 \times [C_6H_5SO_2I]) \geq 1 \times 10^4$. Consequently, it is now apparent that our efforts thus far to attain stereospecificity were all predestined to fall far short of the objective.

Configuration of Free Radicals

Although experiments may be devised which would enable an experimenter to stabilize a radical center before it had racemized, if the radical center is diastereomeric this type of experiment would fail to distinguish between a pyramidal radical and a planar radical which had not yet undergone rotational equilibration. For this reason we have been encouraged to attempt calculations which might cast light on this subject.¹⁸ These calculations involve estimation of valence state energy of a radical carbon and the non-bonding repulsions¹⁹ attributable to the remaining atoms. We find by this method that for a methyl radical, $\cdot CH_3$, ΔE (pyramidal minus planar) ≈ 0 , whereas for the ethyl radical, CH_3-CH_2 , ΔE (pyramidal minus planar) ≈ 3.5 kcal./mole. This difference of 3.5 kcal./mole favoring a pyramidal structure for the ethyl radical results from the non-bonding repulsions of the methyl hydrogens on the methylene hydrogens which is larger in the planar (VI) than in the pyramidal (VII) configuration.



The best geometric description of the bonds to the trivalent carbon of alkyl radicals which are not adjacent to unsaturated groups is that of a low pyramid. If the radicals are not constrained to this position, as in the bridgehead bicyclic radicals, they oscillate rapidly by inversion of the pyramid as in ammonia.²⁰

(16) Irradiation of a solution of benzenesulfonyl iodide, styrene and maleic anhydride in 1:1:1 molar ratio resulted in a good yield of 2-benzenesulfonyl-1-bromo-1-phenylethane. The calculation of a lower limit for the rate of reaction of styryl radical with benzenesulfonyl iodide utilized the values of the absolute rate of addition of a styryl radical to styrene (51.9 l./mole/sec.) and the monomer reactivity ratio for the styrene-maleic anhydride copolymerization system (0.04).

(17) P. S. Skell and A. Y. Garner, *THIS JOURNAL*, **78**, 3410 (1956).

(18) Details will be published elsewhere.

(19) J. O. Hirschfelder and J. W. Linnett, *J. Chem. Phys.*, **18**, 130 (1950).

(20) Recent spectroscopic results are in agreement with the conclusion that for methyl radical ΔE (pyramidal-planar) is small or zero. G. Herzberg and J. Shoosmith (*Can. J. Phys.*, **34**, 523 (1956)), from

Experimental

Materials.—*cis*- and *trans*-2-butene were Phillips Petroleum Co. pure grade, 99 mole % pure. Sulfur dioxide was Virginia Smelting Co., "Extra Dry Esotoo." Bromotrichloromethane was purified by fractional distillation *in vacuo*. See reference 15 for preparation of carbon tetrachloride solutions of benzenesulfonyl iodide.

Potassium bromide (Mallinckrodt, Analytical Reagent) for preparation of specimens for infrared examination of the sulfur dioxide-2-butene copolymers was dried by fusion *in vacuo*.

Sulfur Dioxide-2-Butene Copolymers.—Nitrogen atmosphere was maintained. Pyrex containers were used in all photopolymerizations. Silver nitrate catalyzed polymerizations were carried out in the dark. Close pairing of experiments was maintained for concentrations of reactants, distance from light source and procedure for polymer isolation. Samples of unreacted olefin were isolated by pumping the gases *in vacuo* through a tower of diethanolamine. In all experiments the infrared spectrum of the residual olefin (gas, 100–200 mm., 10-cm. path) was indistinguishable from the spectrum of the starting olefin.

For examination of infrared spectra of the copolymers a sample (1 mg.) was ground with KBr (0.2 g.) and compressed to a transparent disk at 16,000 lb./in.². A similar blank disk was used in the reference beam. Although quantitative work was not feasible in examination of the spectra, particular attention was given to relative peak heights in an effort to detect relative exaltations. The spectra of all copolymers appeared to be identical. The characteristic absorption bands for SO₂-2-butene copolymers are: 3.37(w), 3.42(mw), 6.85(m), 6.90(m), 7.18(w), 7.67(s), 7.92(m), 8.20(mw), 8.76(s), 9.00(ms), 9.53(ms), 10.47(w), 12.00(mw), 13.63(ms, broad) μ .

Competition between Benzenesulfonyl Iodide and SO₂ for *cis*-2-Butene.—Since it has been demonstrated that either *cis*- or *trans*-2-butene reacts with benzenesulfonyl iodide to produce the same mixture of diastereomeric 2-benzenesulfonyl-3-iodobutanes,¹⁵ it was not necessary to use both olefin isomers in carrying out the competitions with SO₂.

In several preliminary experiments it was observed that the insoluble polymer did not begin to separate from the reaction mixture until approximately 40 minutes of irradiation had elapsed. On working up reaction mixtures which had become turbid, small amounts of polymer were separated from the 2-benzenesulfonyl-3-iodobutane by treatment with ethyl ether, a solvent in which the polymer was insoluble.

In 150 ml. of CCl₄ solvent, 5.5 g. of *cis*-2-butene (0.098 mole), 5.1 g. of benzenesulfonyl iodide (0.019 mole) and 7.1 g. of sulfur dioxide (0.119 mole) were irradiated at 0°, in a Pyrex flask located six inches from a 200-watt tungsten filament lamp. At the end of 20 minutes (no turbidity evident) the products were isolated by removing volatile reactants *in vacuo* (0.01 mm.) maintaining a temperature below 20°. The non-volatile residue weighed 5.4 g. A sample of this residue in ether solution was washed with 5% sodium bisulfite to remove any benzenesulfonyl iodide. Evaporation of the ether from the dried solution resulted in recovery of 93% of the original sample. Infrared spectra (neat, or in cyclohexane solvent) of the crude and washed samples were identical except for a trace of CCl₄ in the former. These spectra were also identical with those obtained for the mixture of 2-benzenesulfonyl-3-iodobutanes from the reaction of the 2-butenes with benzenesulfonyl iodide in the absence of SO₂. The characteristic bands for these isomers in CS₂ is published elsewhere.¹⁵ The bands obtained from neat samples are listed, (*) indicating a band not detected or displaced in CS₂: 3.31*, 3.40*, 3.46, 6.32*, 6.77*, 6.92*, 7.24, 7.67, 8.04, 8.46, 8.70, 9.06, 9.23, 9.34, 9.42, 9.61, 9.76, 10.00, 10.17*, 10.55, 11.88, 12.20, 13.10*, 13.78, 14.40*.

UNIVERSITY PARK, PENNSYLVANIA

an analysis of vacuum ultraviolet spectra of $\cdot CH_3$ and $\cdot CD_3$ produced by flash photolyses of Hg(CH₃)₂, CH₃CHO, (CH₃)₂N₂, (CH₃)₂CO, CHI and CH₃Br, concluded $\cdot CH_3$ is either planar or nearly planar. This conclusion is also in agreement with the predictions of molecular orbital theory (A. D. Walsh, *J. Chem. Soc.*, 2296 (1953)).