

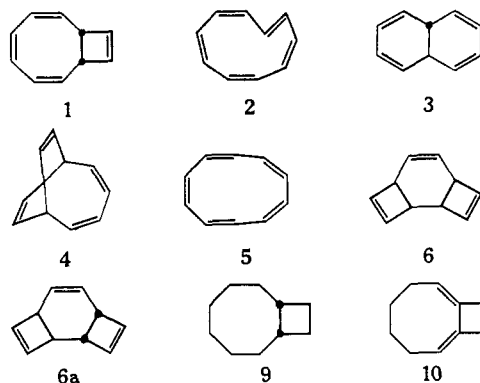
Catalytic hydrogenation of **1** with palladium on carbon or platinum provided quantitatively a saturated hydrocarbon (**9**), $C_{10}H_{18}$ (calcd mol wt, 138.1409; found, *m/e* 138.1409), which was found to be identical (mass, glpc, nmr, infrared) with those obtained by two alternative routes. The bis(dibromocarbene) adduct (mp 93–94°) of cycloocta-1,3-diene was treated with methyl-lithium at -30° to afford through thermally unstable cyclodeca-1,2,4,5-tetraene a good yield of bicyclo[6.2.0]deca-1,7,9-triene (**10**). The latter compound was characterized by its nmr spectrum: τ 3.40 (sharp singlet, 2 H), 4.75–4.95 (triplet, 2 H), 7.7–7.95 (multiplet, allylic 4 H), 8.15–8.55 (multiplet, 4 H). Compound **10** was converted into **9** upon catalytic hydrogenation. Alternatively, pyrolysis of the sodium salt of bicyclo[6.1.0]nonane-9-carboxaldehyde tosylhydrazone¹⁰ at 160° ¹¹ provided, in addition to cyclooctene, bicyclo[6.2.0]dec-9-ene (calcd mol wt, 136.1252; found, *m/e* 136.1250); nmr, τ 4.06 (sharp singlet, 2 H), 7.1–7.4 (broad doublet, 2 H), 8.2–8.7 (multiplet, 12 H). The latter compound was subsequently converted into **9**.¹²

Compound **1** readily and quantitatively isomerized to *trans*-9,10-dihydronaphthalene. The rate of isomerization was measured with an approximately 0.15 *M* solution of **1** in deuteriochloroform and the intensity of the nmr signals at τ 6.32 of **1** and at τ 7.13 of **3** was compared at intervals, using a small sample of methylene bromide as an intensity standard. The isomerization was first order and provided the following kinetic data: $k_{12^\circ} = (6.9 \pm 0.2) \times 10^{-5} \text{ sec}^{-1}$, $k_{70^\circ} = (1.72 \pm 0.05) \times 10^{-3} \text{ sec}^{-1}$. In this temperature range the product **3** was essentially stable and began to change into naphthalene at a measurable rate only above 120° . An obvious proposal for this stereospecific reaction is that the C_1 – C_8 bond opens in a conrotatory process to produce an unstable intermediate **2** (presumably being situated close to the transition state in the energy profile) which cyclizes in a disrotatory process at C_1 and C_6 to form **3**.¹³

Compound **6'** (calcd mol wt, 130.0783; found, *m/e* 130.0783) showed an nmr spectrum consisting of five complex and equally intense multiplets centered around τ 3.32, 4.08, 4.40, 6.85, and 7.53. Upon irradiation (triple) at the last two signals, the absorption at τ 3.32 and 4.40 showed an AX pattern and that at τ 4.08 collapsed to a singlet. Irradiation (triple) at the first and fourth signals produced an almost symmetrical pattern for the second and the last signals, suggesting an AA'XX' system for the latter two sets of protons. These data lead to the proposal of a tentative structure **6** for this compound. The appearance of the diallylic protons at such a high field (τ 7.53) can be rationalized by assigning the *cis,anti,cis* stereochemistry to **6'**, as indicated in **6a**. However, structure **6a** should by no means be taken as established, because other possibili-

ties such as tricyclo[5.3.0.0^{4,8}]deca-2,5,9-triene have not been rigorously excluded.

Photolysis of **1** under similar conditions to those described above¹⁴ produced **4** in addition to other compounds. It is probable that **4** is a secondary reaction product derived from **1**. The photochemical reaction of **1** is highly complex, and we will elaborate on this subject in a separate report.



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(14) Survival of **1** in the photolysis of **7** is due to the formation of insoluble sodium tosylsulfinate, which reduced greatly the transparency of the reaction medium, during the photolysis.

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The Reactions of Sulfur Atoms. X. Addition to Carbon–Carbon Triple Bonds and the Formation of Thiirenes

Sir:

Addition of divalent radicals such as CH_2 ,^{1,2} O atom,^{3,4} and NH^1 to acetylene results in extensive cracking and/or isomerization of the primary adduct even in low-temperature matrices. With dimethylacetylene the primary methylene addition product, dimethylcyclopropene, has been observed,⁵ but the expected primary products of oxygen atom additions, the corresponding oxirenes, have never been obtained. As it appears to date, in spite of the deliberate efforts, the synthesis of the oxirene structure has not been achieved.⁶ For the analogous sulfur compounds, the thiirenes, no reference can be found in the literature.⁷

We have recently examined the reactions of sulfur atoms with acetylenes utilizing a novel technique of

- (1) M. E. Jacox and D. E. Milligan, *J. Am. Chem. Soc.*, **84**, 4080 (1962).
- (2) T. Terao, N. Sakai, and S. Shida, *ibid.*, **85**, 3919 (1963).
- (3) C. A. Arrington, W. Brennen, G. P. Glass, J. V. Michael, and H. Niki, *J. Chem. Phys.*, **43**, 525 (1965).
- (4) I. Haller and G. C. Pimentel, *J. Am. Chem. Soc.*, **84**, 2855 (1962).
- (5) W. von E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960).
- (6) M. Berthelot, *Bull. Soc. Chim. France*, **14**, 113 (1879); R. N. McDonald and P. A. Schwab, *J. Am. Chem. Soc.*, **86**, 4866 (1964); W. Madelung and M. E. Oberwegner, *Ann.*, **490**, 201 (1931); W. G. Dauben, C. F. Hiskey, and M. A. Muhs, *J. Am. Chem. Soc.*, **74**, 2082 (1952); H. Schlubach and V. Franzen, *Ann.*, **577**, 60 (1952); V. Franzen, *Ber.*, **87**, 1479 (1954); J. K. Stille and D. D. Whitehurst, *J. Am. Chem. Soc.*, **86**, 4871 (1964).
- (7) A. Hückel MO calculation by Zahradnik suggests a very low stability for thiirene (R. Zahradnik, *Advan. Heterocyclic Chem.*, **5**, 14 (1965).

(9) L. Skattebol and S. Solomon, *J. Am. Chem. Soc.*, **87**, 4506 (1965).

(10) Prepared from the corresponding carboxylic acid. This acid, prepared from cyclooctene and reported as melting at 113.5–114.8° [S. Akiyoshi and T. Matsuda, *ibid.*, **77**, 2476 (1955)], was found to contain some of the stereoisomer. The pure sample melted at 123.0–123.5°.

(11) W. Kirmse and K.-H. Pook, *Chem. Ber.*, **98**, 4022 (1965).

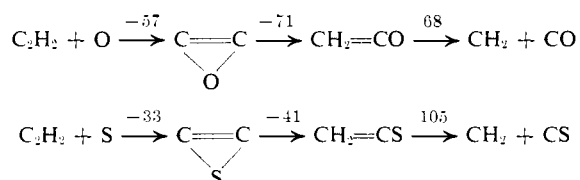
(12) **9** is presumably the same compound as that reported in ref 1f.

(13) Because of lack of molecular symmetry of **1**, **2**, and **3** necessary for the symmetry arguments pertaining to the above modes of isomerization, we cannot apply in a rigid sense the Woodward and Hoffmann rule² to these cases. However, provided that the simple MO calculation gives the correct order for the energy levels of the molecular orbitals of **5** (planar), it is predicted that **1** photolytically opens to give **5** (disrotatory) which closes thermally to *trans*-fused bicyclo[6.2.0]deca-2,4,6,9-tetraene (conrotatory) or *cis*-9,10-dihydronaphthalene (disrotatory).

flash photolysis with kinetic mass spectrometry, which permitted the time-resolved detection and relative concentration measurement of the inherently unstable transient thiirene and its methyl and trifluoromethyl derivatives. A preliminary account of the equipment has been given earlier.⁸

Mixtures of COS (200–400 mtorr) with acetylene (propyne, butyne-2, and hexafluorobutyne-2) (400–800 mtorr) in 14-torr He carrier were flash photolyzed, and time-resolved parent mass intensities of the expected primary adduct were recorded. In each case strong signals were obtained with the following approximate decay half-lives: $C_2H_2S \sim 2$ sec, $C_3H_4S \sim 5$ sec, $C_4H_6S \sim 7$ sec, $C_4F_6S > 0.1$ sec. These long life-time values immediately eliminate excited or radical-like carriers leaving only the thioketene⁹ and thiirene structures as reasonable alternatives. The thioketene formation would require an intramolecular hydrogen, methyl, or trifluoromethyl shift. The hydrogen shift may be facile, but the methyl and especially trifluoromethyl shifts are not; yet product yields appeared to increase with increasing methyl substitution. An additional product observed with the mass spectrometer was thiophene. This compound was also found in the products of conventional photolysis experiments where the yields were 50% for C_4F_6 and 5–10% for the other acetylenes. For thiophene to be formed *via* the ketenes a reversal of the hydrogen or methyl shift would be required. This process should be least likely for perfluorobutyne-2, yet the thiophene yield from this compound is the highest. Thus these findings also support the thiirene *vs.* the thioketene structure for the primary adduct.

A much greater stability of the thiirenes relative to the oxirenes can be predicted on the basis of estimated enthalpy changes (kilocalories/mole) for the reactions



The greater tendency of the oxygen compound for isomerization and cracking is undoubtedly related to the much greater strength of the carbonyl as compared to the thiocarbonyl linkage. Cracking of the thioketene would be endothermic by 31 kcal with ground-state sulfur atoms and 5 kcal with $S(^1D)$ atoms.

If present, the thioketene or its secondary photolysis product, the CS radical, should be detectable by kinetic absorption spectroscopy.¹⁰ Therefore (1:1) mixtures of COS with acetylene and butyne-2 were flash photolyzed and the absorption spectra were recorded photographically. The spectra indicated only trace quantities of CS from the acetylene reaction and no absorbing

(8) W. J. R. Tyerman, W. B. O'Callaghan, P. Kebarle, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **88**, 4277 (1966).

(9) The synthesis of thioketene was reported by H. G. Howard (U. S. Patent 3,035,030 (1962); *Chem. Abstr.*, **57**, 13617f (1962)), but no structural identification was made. The monomer is stable at -80° but polymerizes upon warming.

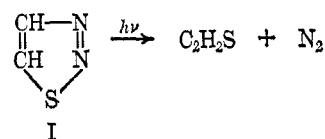
(10) The thiocarbonyl group exhibits relatively strong absorption bands in the visible and near ultraviolet and the thioketene structure should also be a strong absorber. Cf. E. Campaigne in "The Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1966, p 936, and C. N. R. Rao, "Ultraviolet and Visible Spectroscopy," Butterworth and Co. (Publishers) Ltd., London, 1961.

species at all from the butyne-2. Combining all evidence we assign the thiirene structure to the primary adduct.

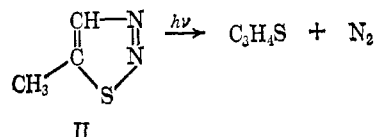
The observation that the cyclic addition product of sulfur atom with acetylene is readily stabilized while the corresponding products of the oxygen and methylene addition are not is in line with the general behavior of the sulfur atom + olefin system. Thus, while the methylene + olefin¹¹ ($\Delta H \sim 80$ kcal) and oxygen + olefin¹² ($\Delta H \sim 84$ kcal) systems readily undergo 1,2 hydrogen (alkyl) shift to yield an olefin or a carbonyl compound, in the sulfur atom + olefin ($\Delta H \sim 60$ kcal) system it has not been possible to find evidence for a similar process.¹³ Since in both the olefin and acetylene systems the isomerization implies a similar 1,2 shift, activation energies should have similar values, probably greater than 60 kcal.

Additional indirect support for the preceding arguments comes from the thermal behavior of the cyclic compounds, cyclopropane,¹⁴ ethylene oxide,¹⁵ and ethylene episulfide.¹⁶ Cyclopropane and ethylene oxide readily transform by 1,2 shift to propylene and acetaldehyde while ethylene episulfide gives only ethylene and sulfur.

The over-all mechanism was further substantiated by photolysis of 1,2,3-thiadiazole (I) and 5-methyl-1,2,3-

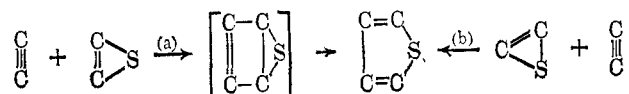


thiadiazole (II). Conventional photolysis gives only



nitrogen, the corresponding acetylene, and a polymeric solid as principal products, but in the presence of perfluorobutyne-2 good yields of the 2,3-bis(trifluoromethyl)thiophenes are obtained.

Thiophene may arise by either of the steps



The reaction of sulfur atom with mixtures of C_2H_2 and perfluorobutyne-2 afforded only the asymmetrical, mixed 2,3-bis(trifluoromethyl)thiophene, favoring path b. Photolysis of I in the presence of perfluorobutyne-2 gave also only 2,3-bis(trifluoromethyl)thiophene. Photolysis of II under similar conditions yielded 2,3-bis(trifluoromethyl)-5-methylthiophene as the sole thiophene product, in agreement with path b. This also sheds further light on the nature of the intermediate since intervention of the ketene structure would be ex-

(11) W. B. De More and S. W. Benson, *Advan. Photochem.*, **2**, 19 (1964).

(12) R. J. Cvetanovic, *ibid.*, **1**, 115 (1963).

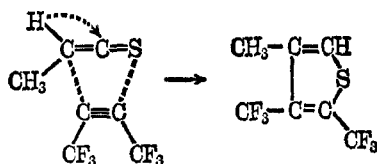
(13) H. E. Gunning and O. P. Strausz, *ibid.*, **4**, 143 (1966).

(14) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

(15) M. L. Neufeld and A. T. Blades, *Can. J. Chem.*, **41**, 2956 (1963).

(16) E. M. Lown, H. E. Gunning, and O. P. Strausz, to be published.

pected to lead to 2,3-bis(trifluoromethyl)-4-methylthiophene formation.



A more detailed account of these studies will be forthcoming.

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Epimerization of 2,4-Diphenylpentane, an Oligomer of Polystyrene

Sir:

The frequency of incidence of the various conformations of a chain molecule such as a vinyl polymer $\text{HCH}_2\text{CHRCH}_2\text{CHR}$ -, etc., or an oligomer thereof, is determined by bond torsional potentials and by interactions between nonbonded atoms. These interactions occur in profusion if R is a group as large as or larger than CH_3 . The same factors must determine the equilibrium distribution among the various diastereoisomers generated by racemization of the asymmetric centers CHR. A statistical mechanical theory of stereochemical equilibrium in chain molecules containing asymmetric centers has been developed recently on this basis.¹ The same parameters that serve to describe the relative proportions of various conformers for a given stereoisomer also define the equilibrium distribution over the various diastereomeric species. Methods for racemization of the asymmetric centers in molecules of the type considered, and for accurate analysis of the equilibrated mixture, are therefore of immediate relevance to investigation of the incidence of various conformations which a given species may assume.

In pursuit of this objective we have succeeded in establishing conditions for equilibration of the *meso* and *dl* isomers of 2,4-diphenylpentane in dimethyl sulfoxide (DMSO) containing potassium *t*-butoxide. The ready occurrence of proton transfer reactions between hydrocarbons under these conditions has been demonstrated in a number of instances.^{2,3} By analogy to these investigations, racemization of the asymmetric centers of 2,4-diphenylpentane may be presumed to occur *via* the formation of a planar alkyl-substituted benzyl anion.² *meso*- and *dl*-2,4-diphenylpentanes were synthesized by the method of Overberger and Bonsignore.⁴ The diastereoisomers were partially separated⁵ and quanti-

tatively determined⁶ by gas chromatography. Nmr spectra⁷ of the compounds agreed with published results.^{8,9} The equilibrium ratios shown in the final column of Table I represent averages of triplicate

Table I. Epimerization of *meso*- and *dl*-2,4-Diphenylpentane

Sample	Initial % <i>meso</i>	Equilibration	
		Time, days	% <i>meso</i>
1	70.0	7	56.5 ^a
2	45.0	14	48.4
3	29.5	14	48.4
4	84.5	28	48.5

^a Not fully equilibrated.

analyses¹⁰ which were in mutual agreement within $\pm 0.5\%$; other values reported are the means of duplicate measurements.

The compounds were epimerized by layering the reagents in a narrow tube in the following order: potassium *t*-butoxide, DMSO, and a mixture of the hydrocarbon with DMSO. The contents were immediately frozen, then degassed, and the tube was sealed. Mixing of the different layers upon gradual warming to room temperature produced a pink color which persisted until the tube was opened and the base destroyed by the addition of water. The color, which disappears rapidly on exposure to air, is indicative of a benzyl anion.¹¹ The hydrocarbon was extracted with pentane, a poor solvent for DMSO, and analyzed. From the final values of the % *meso* given in the last column of Table I, it is evident that the epimerization has reached equilibrium after 14 days and that the same final composition, 48.4% *meso*, is attained from both directions.

In order to confirm that the response of the flame ionization detector used for the gas chromatographic analysis was directly proportional to the concentration of the two isomers, an equilibrated mixture was independently analyzed by taking its nmr spectrum in CCl_4 using the Varian HR-100 spectrometer, the instrument being tuned with special care. The proportions of the two isomers were calculated from the areas of the respective methyl peaks¹² as determined by the triangle approximation. They were also computed from the peak heights. The latter method has been shown to be valid for a series of diastereomeric esters.¹³ Both methods gave $47 \pm 1\%$ *meso* for the composition of the equilib-

(5) Aerograph Model A90-P3 chromatograph, Varian Aerograph Inc., Walnut Creek, Calif. A column, 20 ft \times $\frac{3}{8}$ in., packed with 20% by weight FFAP on Chromosorb W operated at 240° with helium as the carrier gas was used.

(6) Aerograph Model 600-D chromatograph with flame ionization detector. A column, 12 ft \times $\frac{1}{8}$ in., filled with 20% Apiezon-L on acid-washed Firebrick was used. Optimum separation was achieved at 230° with a helium flow rate of 75 cc/min.

(7) Varian A-60 spectrometer operated at room temperature with approximately 20% (w/v) solutions in CCl_4 and tetramethylsilane as reference.

(8) F. A. Bovey, F. P. Hood III, E. W. Anderson, and L. C. Snyder, *J. Chem. Phys.*, **42**, 3900 (1965).

(9) D. Lim, B. Obereigner, and D. Doškočilová, *J. Polymer Sci.*, **B3**, 893 (1965).

(10) Calculations of the two isomers based on the areas of the respective peaks measured with a planimeter.

(11) G. A. Russell and A. G. Bemis, *J. Am. Chem. Soc.*, **88**, 5491 (1966).

(12) The methyl doublets of *meso*- and *dl*-2,4-diphenylpentane are centered respectively at δ 1.20 and 1.15.

(13) J. A. Dale and H. S. Mosher, to be published.

(1) P. J. Flory, *J. Am. Chem. Soc.*, **89**, 1798 (1967).

(2) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965.

(3) J. E. Hoffman, R. J. Muller, and A. Schriesheim, *J. Am. Chem. Soc.*, **85**, 3002 (1963).

(4) C. G. Overberger and P. V. Bonsignore, *ibid.*, **80**, 5427 (1958).