I

II

III

IV

such as those of 8,8-dicyanoheptafulvene (τ 2.8), tropone (τ 3.0), and heptafulvalene (τ 4.2).[5] The downfield shift of the π-cyclopentadienyl proton absorption in the nmr and the shift of the carbonyl bands to higher wavelength following hydride abstraction both indicate more positive charge residing on the iron atom in the product relative to the starting σ complex II; however, the magnitudes of the shifts are not so great as those normally observed for this σ- to π-bonded ligand transformation.[7]

The heptafulvene complex did not form an adduct with tetracyanoethylene on standing at room temperature in solution for several hours, and it was resistant to hydrogenation (unchanged after 24 hr at 25° over Pd–C, 45 psi of H_2). Treatment with $NaBH_4$ gave a mixture of the tautomers of the starting σ complex II;[12] treatment of this mixture with $(C_6H_5)_3C^+SbF_6^-$ regenerated the heptafulvene complex.

Since esters of 7-(hydroxymethyl)cycloheptatriene had been shown to undergo ring contraction on solvolysis,[8] and in order to prepare a model compound for spectral comparison to the heptafulvene complex, σ-(2-phenylethyl)-π-cyclopentadienyliron dicarbonyl (V) was prepared in 80% yield from (2-bromoethyl)benzene and $Na[Fe-\pi-Cp(CO)_2]$. The product was a yellow, air-stable[13] solid, mp 73–74°, with a cyclopentadienyl proton absorption at τ 5.44 (CS_2), and carbonyl absorptions in the infrared at 1942 and 2000 cm^{-1} (CH_2Cl_2). When $(C_6H_5)_3C^+PF_6^-$ was added to V in CH_2Cl_2, the yellow styrene complex (VI),[13] clearly different from the heptafulvene complex, was immediately precipitated. The nmr absorption of the cyclopentadienyl protons (τ 4.13 in acetone, relative to TMS) and the infrared absorptions of the iron carbonyl groups (2020 and 2062 cm^{-1}, CH_2Cl_2 or Nujol) are as expected for structure VI.[7]

The spectral data for the heptafulvene complex fall at positions intermediate between those expected for III

(12) Cais has reported similar results in the reduction of his complexes; see ref 3.
(13) Satisfactory analytical data were obtained for this compound.

V

VI
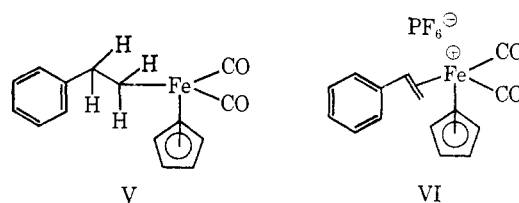
and for IV[14] and do not therefore provide clear differentiation between these possibilities. An intermediate structure, such as one based on IV, but having extensive delocalization of positive charge into the iron,[15] may be in best agreement with the available data.[16] Studies are now under way directed toward a resolution of this question as well as to liberation of free heptafulvene from the complex.

(14) The nmr absorption at τ 2.20 indicates considerable shielding of the ring protons as compared to the unsubstituted tropylium fluoroborate at τ 0.86 (G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, J. Am. Chem. Soc., 82, 5846 (1960)) or to cyanomethyl-tropylium fluoroborate at τ 0.78.[6]
(15) This may occur through carbon–iron hyperconjugation, or by direct interaction of the metal orbitals with those of the seven-membered ring. For a discussion of these types of metal–carbon interactions, see T. G. Traylor and J. C. Ware, J. Am. Chem. Soc., 89, 2304 (1967).
(16) Such an intermediate structure has been observed for a styrene-palladium chloride complex: J. R. Holden and N. C. Baenziger, J. Am. Chem. Soc., 77, 4987 (1955). We thank a referee for calling this precedent to our attention.
(17) Deceased March 20, 1968.

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Transition-State Geometry of a (2 + 2) Cycloaddition Reaction. Asymmetric Synthesis in a Sulfene–Enamine Condensation[1,2]

Sir:

Although the subject of considerable study since its recognition many years ago, the phenomenon of asymmetric induction[3] has never been applied to the synthesis of four-membered rings, whether carbocyclic or heterocyclic.[4] Recently, interest in the stereochemical consequences of (2 + 2) cycloaddition reactions has been on the increase in view of the interesting predictions provided by the Woodward–Hoffmann rules for such reactions.[5] The present communication describes an example of asymmetric synthesis in the preparation of a thiete 1,1-dioxide and represents a continuation of our studies on the chemical behavior of sulfenes.[6]

(1) Unsaturated Heterocyclic Systems. LXIX. For the previous paper in this series, see L. A. Paquette, R. W. Houser, and M. Rosen, J. Org. Chem., in press.
(2) Partial financial support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (Grant GP-5977) is gratefully acknowledged.
(3) The principle of asymmetric synthesis has recently been reviewed: (a) D. R. Boyd and M. A. McKervey, Quart. Rev. (London), 22, 95 (1968); (b) J. Mathieu and J. Weill-Raynal, Bull. Soc. Chim. France, 1211 (1968).
(4) A review of the formation of four-membered heterocycles has recently appeared: L. L. Muller and J. Hamer, "1,2-Cycloaddition Reactions," Interscience Publishers, New York, N. Y., 1967.
(5) R. Hoffmann, Abstracts of the Twenty-First National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, 1969, pp 109–129.
(6) L. A. Paquette, J. P. Freeman, and R. W. Houser, J. Org. Chem., 34, 2901 (1969); L. A. Paquette and R. W. Begland, ibid., 34, 2896 (1969); L. A. Paquette and M. Rosen, J. Am. Chem. Soc., 89, 4102 (1967), and earlier references contained in these papers.

(R)-(+)-Methyl-α-phenethylamine (1), [α]²²D +62.7 ± 0.5° (c 3.989, C₂H₅OH), of established absolute configuration was prepared by the reaction of (R)-(+)-α-phenethylamine[7] with formyl acetic anhydride and reduction of the resulting formamide with lithium aluminum hydride.[8] Conversion of 1 to enamine 2, [α]²⁰D +43.5 ± 0.5° (c 1.932, CHCl₃), was achieved in 68% yield by condensation with propionaldehyde in tetrahydrofuran containing anhydrous potassium carbonate (Scheme I). The trans geometry of the enamine

Scheme I

1

2

3

4

(+)-5
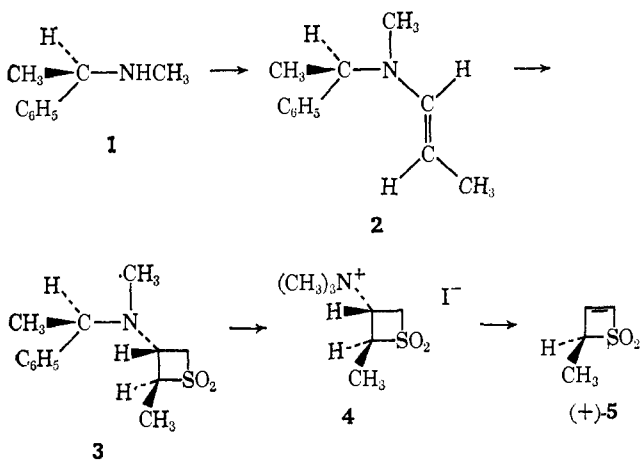
double bond in 2 was clearly revealed by its nmr spectrum in which the two vinyl protons were seen to be spin coupled by 13.2 Hz. Treatment of 2 with sulfene, generated from methanesulfonyl chloride and triethylamine in anhydrous ether at −5°, afforded an oily mixture of diastereomers of 3,[9] which was directly heated with excess methyl iodide in acetone at 67° for 20 hr. This convenient debenzylation procedure, which permitted ready removal of the original asymmetric carbon atom, gave methiodide 4 (dl isomer, mp 196–197° dec) in 36% overall yield from 2. Although the nmr spectra of 3 and 4 were complex, the data are in agreement with the trans stereochemical assignment which, additionally, follows from earlier precedent.[11]

Crude 4, which was noted to be optically active, was treated directly with dry silver oxide in anhydrous tetrahydrofuran to which had been added some calcium sulfate (10–20 mesh). This modification of the Hofmann elimination procedure gave (62% yield) 4-methylthiete 1,1-dioxide (5) containing no more than 7 ± 1% (nmr analysis)[12] of the more stable, but optically inactive, 2-methylthiete 1,1-dioxide (6). Allowing for this extent of contamination, 5 was found to exhibit an optical rotation of [α]¹⁹D +1.32 ± 0.51° (c 6.065, CHCl₃). A

near identical value was realized from a duplicate series of experiments. Great care was exercised at each step of Scheme I to avoid accidental separation of diastereomers. When such conditions were not met, the optical purity of 5 was seen to increase approximately tenfold.

The synthesis of 4-methylthiete 1,1-dioxide of maximum rotation began with the preparation of trans-2-methyl-3-piperidinothietane 1,1-dioxide d-camphor-10-sulfonate. Four successive recrystallizations of this salt from absolute ethanol gave solid, mp 244.5–246° dec,[13] from which pure 7, mp 54.5–56°, [α]²²D +70.0 ± 0.3° (c 3.100, C₂H₅OH), was obtained. Quaternization of this material gave in essentially quantitative yield the methiodide 8, mp 196–197.5° dec, [α]²¹D +21.6 ± 0.2° (c 4.829, H₂O) (Scheme II), Hofmann elimina-

Scheme II

7, R = —N⟨ ⟩

8, R = —N⁺⟨ ⟩ I⁻
     |
     CH₃

(−)-9

(+)-10
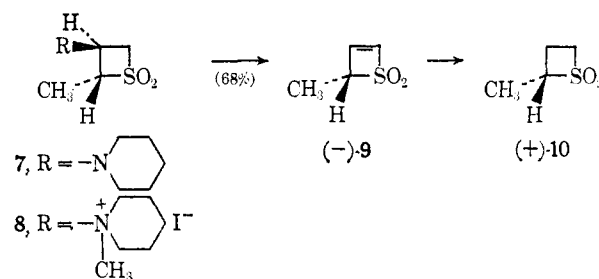
tion of which in the predescribed manner yielded white crystalline (mp 59.5–61.5°) levorotatory sulfone 9, [α]²¹·⁵D −21.2 ± 0.4° (c 5.995, CHCl₃). Submission of pure 9 to catalytic hydrogenation afforded 2-methylthietane 1,1-dioxide 10, [α]²¹·⁵D +21.0 ± 0.2° (c 9.740, C₂H₅OH). On this basis, the asymmetric induction experiments (Scheme I) are seen to produce 5 which is 6% enriched in the amount of (+) isomer.

Since the primary theoretical interest resides not only in the magnitude, but also in the direction, of the stereoselectivity of attack of sulfene upon the enamine, the absolute configurations of (+)- and (−)-2-methylthietane 1,1-dioxides were determined. To this end, (S)-(+)-β-acetoxybutyric acid (11), [α]²⁴D +3.6 ± 0.3° (c 10.175, C₂H₅OH), of known absolute configuration[14] was obtained by partial resolution of the dl isomer with quinine. Reduction of 11 to (S)-(+)-1,3-butanediol (12), [α]²⁴D +10.1 ± 0.5° (c 10.17, CHCl₃),[14a,15] with lithium aluminum hydride was followed by dimesylation and direct exposure of 13 to the action of lithium bromide in refluxing dioxane (Scheme III). This series of transformations was completed by conversion of the resulting (R)-bromide 14, [α]²⁵D −29.9 ± 0.5° (c 17.780, CHCl₃), to (S)-2-methylthietane (15) with thiourea in aqueous sodium hydroxide, and oxidation of this sulfide to its sulfone (16). In view of the double SN2 displacement which intervenes in the passage from 13 to 15, the asymmetric carbon in 16 must be of the S configuration. Since 16 was found to be levorotatory, [α]²⁴D −8.4 ± 0.7° (c 5.620, C₂H₅OH), sulfones 9 and 10 must be in the R series. It now follows that, because 5 is dextrorotatory, the ab-

(7) [α]²¹D +29.2 ± 0.2° (c 12.56, C₂H₅OH), [α]²¹D +38.9° (neat). For the absolute configurational assignment, see G. Fodor and G. Csepreghy, Tetrahedron Lett., No. 7, 16 (1959).

(8) For the preparation of the dl isomer, cf. C. F. Heubner, E. M. Donoghue, A. J. Plummer, and P. A. Furness, J. Med. Chem., 9, 830 (1966).

(9) Chromatographic purification of a dl sample of 3 gave a white solid, mp 70–85°.[10]

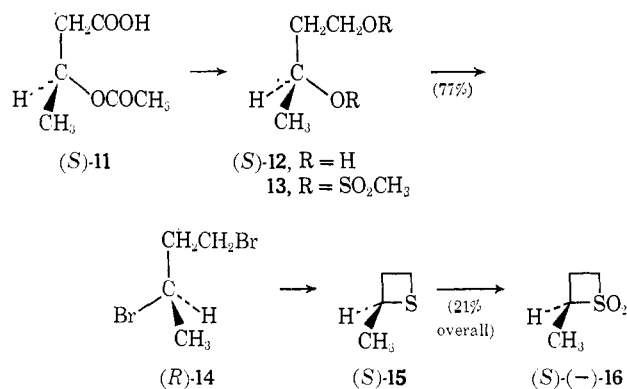(10) All new compounds were analyzed as their dl isomers; acceptable values (±0.3 %) were obtained in all cases.

(11) Note particularly G. Opitz, Angew. Chem. Intern. Ed. Engl., 7, 646 (1968).

(12) For 5: δ$_{TMS}^{CDCl_3}$ 7.07 (dd, J = 4 and 1.9 Hz, H₃), 6.70 (d, J = 4 Hz, H₂), 4.83 (qd, J = 7 and 1.9 Hz, H₄), and 1.54 (d, J = 7 Hz, CH₃). 2-Methylthiete 1,1-dioxide (6) is readily available from the silver oxide induced Hofmann elimination of dl-8 in water solutions: δ$_{TMS}^{CDCl_3}$ 6.80 (m, H₃), 4.40 (m, 2 H, H₄), and 2.03 (m, 3 H, CH₃).

(13) Additional recrystallizations from ethanol and acetonitrile failed to increase further the melting point of this salt or the optical rotation of free amine 7.

(14) (a) K. Serck-Hanssen, Arkiv Kemi, 8, 401 (1955); (b) K. Serck-Hanssen, S. Stallberg-Stenhagen, and E. Stenhagen, ibid., 5, 203 (1953).

(15) R. Lukes, J. Jary, and J. Nemec, Collection Czech. Chem. Commun., 27, 735 (1962).

Communications to the Editor

Scheme III

(S)-11   (S)-12, R = H
13, R = SO$_2$CH$_3$

(R)-14   (S)-15   (S)-(−)-16

solute configuration of favored enantiomer (+)-**5** produced in the sulfene–enamine condensation is established as S.

In light of the above data, it is clear that asymmetric induction in (2 + 2) cycloadditions can be achieved. Attempts to increase the extent of stereoselectivity by structural modification of the amine and other means is presently receiving attention. Discussion of the observed stereoselectivity in terms of transition-state theory is deferred to the full paper.

(16) American Chemical Society Petroleum Research Fund Graduate Fellow, 1968–1969; National Science Foundation Graduate Fellow, 1966–1968.

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Photochemistry of (S)-(+)-5-Methyl-2-heptanone

Sir:

The photochemistry of alkanones with γ hydrogens is interesting from a mechanistic point of view in that their reactions may take place from their singlet state as well as from their triplet state. The reactions proceed with moderate quantum yields, e.g., 0.34 ± 0.01 for 2-hexanone, and the principal products are those derived from the type II process and cyclobutanols.

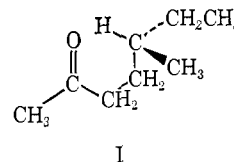Compound I was synthesized from (S)-(+)-1-bromo-3-methylpentane[2] by addition of the corresponding Grignard reagent to acetic anhydride[3] and purified through its semicarbazone to give a product of 99.4% purity as indicated by vpc, bp 77–78° (40 mm), [α]^{25}D

I

+9.84°, semicarbazone mp 133–134°.

As expected, irradiation of I in either hexane or t-butyl alcohol in the presence or absence of cis-1,3-pentadiene gave acetone, 2-methyl-1-butene, and a mixture of cyclobutanols as the major products. A very small amount of 5-methyl-2-heptanol was also detected when the irradiation was carried out in hexane but not in t-butyl alcohol or in hexane with pentadiene. Each solution was 1.0 M in I. The irradiating wavelength was 313 nm, carried out on an apparatus previously described.[4] Quantum yields for the disappearance of ketone, the formation of acetone, and the formation of the cyclobutanols were determined using 2-hexanone as a secondary actinometer. Quantum yields for racemization were determined by recovering the irradiated ketone by vpc, measuring the change in optical rotation at four wavelengths between 220 and 305 nm on a Cary 60 spectropolarimeter, and relating the amount of racemate formed to the quantum yield for the disappearance of ketone and the per cent conversion. The results of the irradiation under various conditions are summarized in Table I.

From the results we find two observations interesting. (1) Although the photochemical reactions of I proceed with concurrent racemization in both hexane and t-butyl alcohol, the reactions in the presence of pentadiene, i.e., those from the singlet state, do not proceed with racemization. Therefore, the racemization must take place from the triplet state. The results suggest that

Table I

Solvent	$\phi_{-ketone}$	$\phi_{type\ II}$	$\phi_{cyclobutanols}$	$\phi_{racemization}$	$\phi_{photoreduction}$
Hexane	0.158 ± 0.003	0.128 ± 0.003	0.025 ± 0.001	0.08 ± 0.02	0.0040 ± 0.0005
t-Butyl alcohol	0.18 ± 0.04	0.157 ± 0.004	0.029 ± 0.002	0.04 ± 0.02	
Hexane + 2.5 M cis-1,3-pentadiene	0.073 ± 0.002	0.071 ± 0.002	0.006 ± 0.001	0.002 ± 0.010^a	<10$^{-4\,a}$
t-Butyl alcohol + 2.5 M cis-1,3-pentadiene	0.07 ± 0.02	0.058 ± 0.001	0.004 ± 0.001		

^{a} In 5.0 M cis-1,3-pentadiene.

Wagner[1] has suggested that the triplet state of ketones with γ hydrogens will give a biradical intermediate first which may revert to the starting ketone or proceed to give products in nonpolar solvents, while in polar solvents it will proceed to give products predominantly. Therefore, the reactions may involve a vibrationally excited ground state as well. In order to achieve a better understanding of the relative roles of the excited states and the nature of the nonradiative decay processes in the photochemistry of alkanones with γ hydrogens, (S)-(+)-5-methyl-2-heptanone (I) was synthesized and its photochemistry investigated.

(1) P. J. Wagner, J. Amer. Chem. Soc., **89**, 5898 (1967).

the reactions from the singlet and the triplet state of I take place via different mechanisms. (2) The reactions proceed with higher quantum yields in t-butyl alcohol than in hexane, and the increase in quantum yield is the same as the decrease in racemization within experimental error. The combined quantum yields of observed events in t-butyl alcohol are about 0.2, which falls far short of 1.0 as found in the case of analogous aromatic ketones.[1]

Our results provide support for Wagner's theory that the ^{3}n,π* state of I will decay via a biradical interme-

(2) H. S. Mosher and E. La Combe, ibid., **72**, 4991 (1950).
(3) M. S. Newman and W. T. Booth, Jr., ibid., **67**, 154 (1945).
(4) D. R. Coulson and N. C. Yang, ibid., **88**, 4511 (1966).