Table II. Effect of the Metal Oxidant on the Ratio of Oxidation Products to Cyclized Ketone

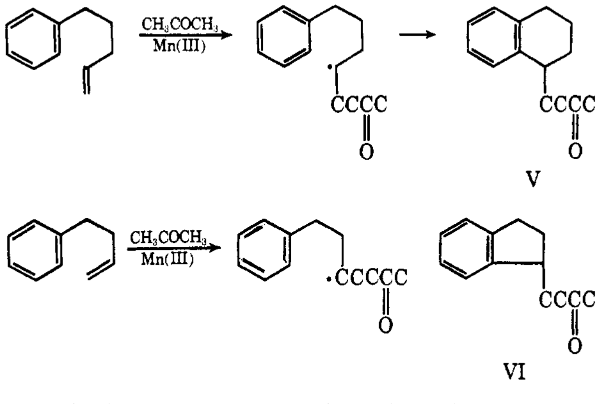
[Oxidant], *M*	(II + III)/IV
Mn(III), 0.11	0.13
Mn(III), 0.23	0.23
Ce(IV), 0.017	0.19
Ce(IV), 0.034	0.35
Cu(II), 0.0039, + Mn(III), 0.10	0.85

ever, decreased linearly as the metal ion concentration increased, as shown in Figure 1 and Table II. These observations are all consistent with the proposed scheme in which products I and IV are produced *via* a free-radical pathway.

The relative rates of oxidation of the radical A by Mn(III), Ce(IV), and Cu(II) as estimated from Table II indicate that Cu(II) is a stronger oxidant than Ce(IV), which in turn is a stronger oxidant than Mn(III).[1]

From Figure 1 the bimolecular rate of oxidation of radical A by Cu(II) relative to the rate of internal radical cyclization was found to be 240 at 25°. This high rate of oxidation of radical A by cupric acetate relative to internal cyclization is comparable to that reported for the cyclization of the δ-phenylbutyl radical[3] to tetralin (350). The lower value obtained here is most probably due to a more rapid rate of cyclization of the tetralone precursor, due to stabilization of the cyclohexadienyl radical intermediate by the carbonyl group, rather than to differences in radical oxidation rates.[4] Assuming the rate of radical oxidation by cupric acetate to be approximately $7.6 \times 10^7\ M^{-1}\ \text{sec}^{-1}$, which is the value reported[4] for the secondary butyl radical at 57°, the rate of internal cyclization of radical A can be calculated to be about $3 \times 10^5\ \text{sec}^{-1}$, which is comparable to other reported rates of radical cyclization.[5]

Another variation of the synthesis of a cyclized product utilizing the reaction of a ketone with an olefin in the presence of Mn(III) or Ce(IV) is exemplified by the reaction of acetone with 5-phenylpentene-1, which gave the tetralin V as the predominant product in 70% yield. 4-Phenylbutene-1, however, gave only minor amounts of the cyclized product VI as shown in Table III. As expected, the two adduct radicals had similar rates of oxidation by Mn(III) and hydrogen abstraction as shown in the last column in Table III. The difference in behavior of these two olefins, therefore, was due to the difference in the rates of cyclization of the two radical intermediates, which, in the case of the six-membered ring, is some 55–65 times greater than the rate of cyclization to form an indan.[6]



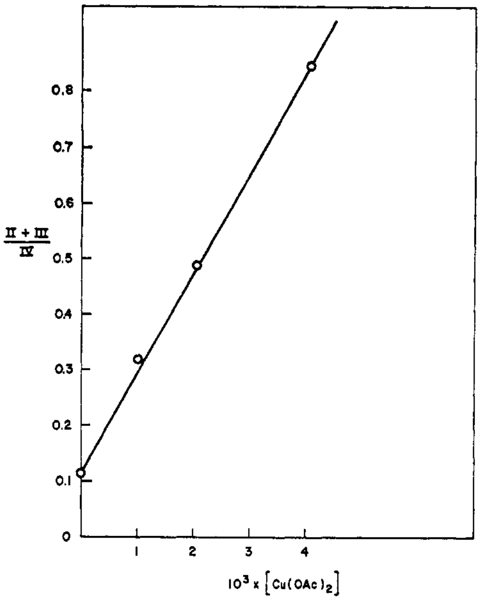


Figure 1. Effect of added cupric acetate on the product ratio.

Table III. Product Ratios of the Reactions of Aromatic Olefins with Acetone

Olefin^a	Ox^b/(V or VI)	S^c/(V or VI)	Ox^b/S^c
$C_6H_5(CH_2)_3CH{=}CH_2$	0.20	0.12	1.5
$C_6H_5(CH_2)_2CH{=}CH_2$	11.0	7.8	1.4

^{a} Identical reaction conditions, 45°, $[\text{Mn(III)}]_{\text{av}}$ = 0.09 *M*. ^{b} Ox = unsaturated ketone + keto ester. ^{c} S = saturated noncyclic ketone.

Acknowledgment. The authors are indebted to Dr. P. G. Rodewald for the synthesis of some cyclic ketones, and to Mr. G. E. Stead for skillful assistance in carrying out the reported experiments.

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Received January 10, 1972

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[3] J. K. Kochi and R. D. Gilliom, *J. Amer. Chem. Soc.*, **86**, 5251 (1964).

[4] J. K. Kochi and R. V. Subramanian, *ibid.*, **87**, 4855 (1965).

[5] D. J. Carlsson and K. U. Ingold, *ibid.*, **90**, 7047 (1968).

[6] W. H. Urry, D. J. Trecker, and H. D. Hartzler, *J. Org. Chem.*, **29**, 1663 (1964).

"Through-Space" Coupling between Bucking Fluorine and Hydrogen Nuclei in *trans*-1,1′-Difluorotetrabenzopentafulvalene[1]

Sir:

Recently, compelling evidence has been put forward in favor of a "through-space" ("direct") mechanism operating in long-range proton–fluorine spin–spin coupling in a series of bridged biphenyls and phenan-

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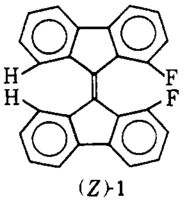
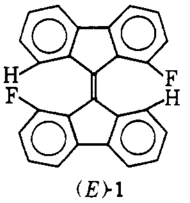
[1] Fulvenes and Thermochromic Ethylenes. 64. For part 63 see E. D. Bergmann and I. Agranat, *J. Chem. Soc. C*, 3532 (1971).

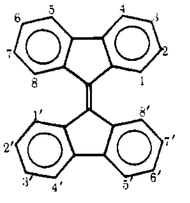
threnes.[2] The spatial structures in these rare cases had been estimated beforehand. In particular, the short internuclear distance between the interacting nuclei, fluorine, and methyl proton served as a basis for the firm establishment of the through-space mechanism. We wish to report the phenomenon of through-space H–F coupling ($^7J_{H-F}$) in *trans*-1,1′-difluorotetrabenzopentafulvalene ((*E*)-**1**) and its significant contribution toward the endeavor to shed light upon the spatial structure of the highly controversial parent compound tetrabenzopentafulvalene (**2**).[3]



(*Z*)-1



(*E*)-1



2

1,1′-Difluorotetrabenzopentafulvalene (**1**) was synthesized in the following manner, applying conventional methods:[3b] zinc–ammonia reduction of 1-fluoro-9-fluorenone[4] in boiling ethanol gave 1-fluoro-9-fluorenol (mp 116°),[5] which was converted to 9-bromo-1-fluorofluorene (mp 93°)[5] by hydrobromic acid (48%) in acetic acid at 60°. Treatment of the latter with Triton B (40% in methanol) in *p*-dioxane at 24° afforded the desired compound **1**, as red needles: mp 208°;[5] $\lambda_{max}^{C_6H_{12}}$ (log ϵ) 245 nm (4.88), 271 (4.50), 312 (3.41), 351 s (3.61), 369 (3.66), and 453 (4.43).

1 exists in two geometrical forms, the cis isomer ((*Z*)-**1**) and the trans isomer ((*E*)-**1**), as revealed by the ^{1}H and ^{19}F magnetic resonance spectra:[6] pmr δ^{CDCl_3} 8.38 (m, *ca.* 1 H), 7.68 (m, 2 H), 7.47 (m, *ca.* 3 H), 7.28 (m, 6 H), and 6.94 ppm (m, 2 H). The low-field ^{1}H multiplet at δ 8.38 ppm, which is characteristic of the protons ortho to the "pinch" of the tetrabenzopentafulvalene system (H-8 and H-8′),[3c] corresponds to only 43% of the calculated value (two ortho protons *vs.* 12 remaining protons). This absorption can appear only in the spectrum of (*Z*)-**1**, which resembles in this respect the parent compound **2**. In the spectrum of (*E*)-**1**, due to the shielding effect of each fluorine nucleus upon its bucking proton, the low-field absorption is shifted to the normal aromatic region. Thus, the pmr spectrum of **1** points to a mixture of 43% of (*Z*)-**1** and 57% of (*E*)-**1**. Both the chemical shift and the pattern of the multiplet at 6.94 ppm indicate that it represents the protons ortho to the fluorine in both isomers, H-2 and H-2′. The multiplet at 7.68 ppm represents the angular protons H-5 and H-5′ (in both isomers).[7] The other angular protons, H-4 and H-4′, are shifted to a higher field, due to the effect of the para fluorine atoms, and are included in the 7.47 multiplet. It is the only one (apart from the low-field multiplet) which represents (approximately) an odd number of protons; it must therefore include the absorption due to H-8 and H-8′ of (*E*)-**1**. The last multiplet, at 7.28 ppm, represents H-3, H-6, H-7, H-3′, H-6′, and H-7′.[7] The pmr spectrum of **1** in C_6D_6 reveals the absorption representing H-8 and H-8′ of (*E*)-**1** as a separate multiplet, at 7.60 ppm.

The above interpretation is confirmed by the ^{19}F magnetic resonance spectrum[6] (C_6D_6) of **1**, which contains two signals, at 9080 and 9600 Hz in the ratio of 3:4. The low-field signal represents the fluorine atoms of (*E*)-**1**. In (*Z*)-**1**, the two bucking fluorine nuclei shield each other, thus shifting the fluorine absorption to a higher field.

The most striking feature in the spectra of **1** is the difference in the pattern of the two fluorine multiplets. While the multiplet attributed to (*Z*)-**1** appears to be "normal" (resembling, *e.g.*, the ^{19}F nmr spectra of 9,9-dichloro-1-fluorofluorene and 9-bromo-1-fluorofluorene), the multiplet attributed to (*E*)-**1** reflects an additional nonnegligible coupling (J = 7 Hz). We submit that this phenomenon must be rationalized in terms of a "through-space" ("direct") spin–spin coupling, operating between the bucking nuclei, F-1 *vs.* H-8′ and F-1′ *vs.* H-8 in *trans*-1,1-difluorotetrabenzopentafulvalene ((*E*)-**1**). This conclusion was verified by proton–fluorine decoupling experiments (in C_6D_6). The ^{19}F–{^{1}H} proton-decoupled spectra indicated the following. (1) Double irradiation at 6.94 ppm (nullifying the $^3J_{H-F}$ coupling due to H-2 and H-2′ in both isomers), collapsed the 9600-Hz signal to a singlet, and transferred the 9080-Hz multiplet into a doublet (J = 7 Hz). (2) Double irradiation at 7.60 ppm (nullifying the through-space coupling due to H-8 and H-8′ of (*E*)-**1**) transformed the low-field signal into a quartet (J_1 = 9 Hz, J_2 = 4 Hz), while the high-field signal remained unaltered. The ^{1}H–{^{19}F} fluorine-decoupled spectra exhibited a simplification of the 7.60-ppm multiplet (into a "quartet") only by irradiation at 9080 Hz.

The existence of a substantial through-space coupling between F-1 and H-8′ in (*E*)-**1** reflects the short distance between the interacting nuclei. This in turn implies a ground-state conformation in which the deviation from planarity is rather small. Particularly, if the molecule, in order to relieve the "overcrowding" around the "pinch," adopts a twisted conformation, the twist must be limited to a degree which still permits the through-space H–F coupling to operate. This coupling, which has the largest $^7J_{H-F}$ yet observed, results from interactions centered not on fluorine and methyl carbon nuclei,[2] but directly between fluorine and hydrogen nuclei.

In the closely related 1,1′-difluoro-6,6′-diisopropylbianthrone,[8] there exists no evidence of a through-space H–F coupling. The ^{19}F spectrum (CH_2Cl_2) shows two "normal" multiplets at 10,083 and 10,347 Hz,[6] indicating the presence of two geometrical isomers. The conformations of both deviate considerably from

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(2) (a) G. W. Gribble and J. R. Douglas, *J. Amer. Chem. Soc.*, **92**, 5764 (1970); (b) K. L. Servis and F. R. Jerome, *ibid.*, **93**, 1535 (1971), and references cited therein.

(3) (a) E. Bergmann and A. Weizmann, *Chem. Rev.*, **29**, 575 (1941); (b) E. D. Bergmann, *Progr. Org. Chem.*, **3**, 81 (1955); (c) M. Rabinovitz, I. Agranat, and E. D. Bergmann, *Tetrahedron Lett.*, 1265 (1965); (d) E. D. Bergmann, *Chem. Rev.*, **68**, 41 (1968); (e) I. R. Gault, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc. D*, 269 (1970); (f) N. A. Bailey and S. E. Hull, *ibid.*, 960 (1971).

(4) T. L. Fletcher and M. J. Namkung, *Chem. Ind.* (*London*), 179 (1961).

(5) All new compounds have been fully characterized (combustion analyses, ir, uv, mass spectra).

(6) The ^{1}H and ^{19}F nmr spectra were recorded at 100 and 94.1 MHz, respectively. ^{1}H chemical shifts are reported in parts per million downfield from Me_4Si. ^{19}F chemical shifts are reported in hertz upfield from CCl_3F.

(7) (a) K. D. Bartle and D. W. Jones, *J. Mol. Struct.*, **1**, 131 (1967–1968); (b) M. Rabinovitz, I. Agranat, and E. D. Bergmann, *J. Chem. Soc. B*, 1281 (1967).

(8) E. D. Bergmann, H. Weiler-Feilchenfeld, A. Heller, C. Britzmann, and A. Hirschfeld, *Tetrahedron, Suppl.*, No. 7, 349 (1966).

planarity; even in the trans isomer, F-1 is never in proximity to H-8′.

The fluorine signals of **1** did not coalesce even at 220°. This behavior contrasts sharply with the ease of the cis–trans isomerization of 1,1′-dialkoxycarbonyl derivatives of **2**.[3e] Undoubtedly, such bulky substituents, through their contribution to the ground-state strain, lower substantially the activation energy for the interconversion of the geometrical isomers. The energy barriers associated with the cis–trans isomerization of **1**, in which the ground-state strain is much diminished, are significantly higher.

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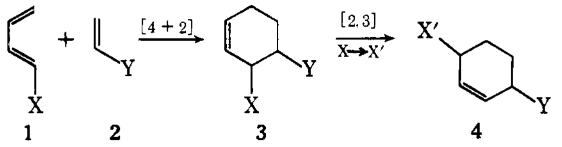
Received December 3, 1971

The Complementarity of (4 + 2) Cycloaddition[1] Reactions and [2,3] Sigmatropic Rearrangements in Synthesis. A New Synthesis of Functionalized Hasubanan Derivatives

Sir:

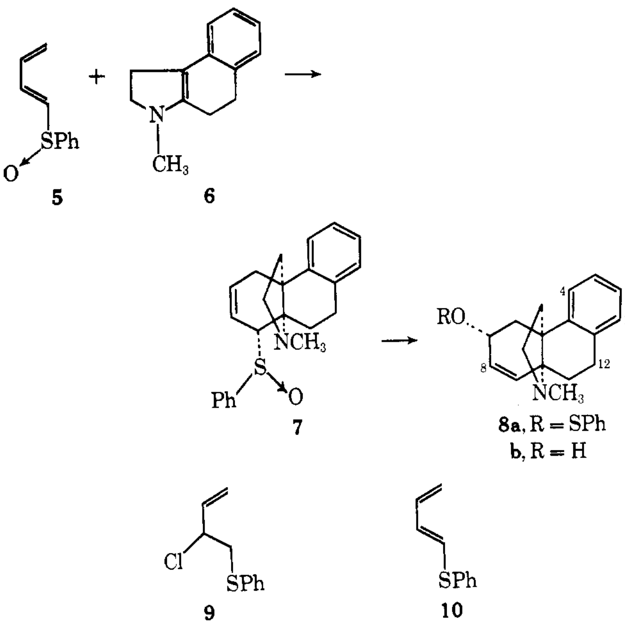
Although a number of elegant rearrangements generally classified as [2,3] sigmatropic processes have recently been reported,[2] the incorporation of this class of reactions into synthetic methodology has been quite limited.[3] The purpose of this communication is to define the complementary nature of certain (4 + 2) cycloaddition and [2,3] sigmatropic reactions. As illustrated in Scheme I, the merging of these two processes leads to substituted cyclohexene derivatives such as **4** which may be relatively inaccessible *via* the direct cycloaddition route.

Scheme I



In the course of our current work directed toward the synthesis of both the hasubanan and morphine bases,[4] an annelation sequence like that depicted in Scheme I appeared to offer an attractive solution to the construction of hasubanan derivatives (*cf.* **8b**) embodying a ring-C oxidation pattern common to both classes of alkaloids. The application of this merged cycloaddition–rearrangement process as applied to the synthesis of the tetracyclic amino alcohol **8b** is illustrated in Scheme II.

Scheme II



The pivotal feature in the annelation scheme depicted above involves the conversion of sulfoxide **7** into allylic alcohol **8b**, a transformation which relies upon the interception of the corresponding sulfenate ester **8a** with appropriate thiophilic reagents.[3a,b] In an effort to test the viability of this proposed sequence a synthesis of the previously unreported 1-butadienyl phenyl sulfoxide (**5**) was undertaken. The addition of phenyl sulfenyl chloride to butadiene cleanly afforded the chloro sulfide **9** in greater than 90% yield.[5] Subsequent dehydrohalogenation of **9** with potassium *tert*-butoxide in THF at 0° gave the *trans*-dienyl sulfide **10** as a colorless liquid (bp 50–53° (0.04 mm)) in 60% yield.[6,7] Although **10** has been synthesized by an alternate procedure,[7] the present route is decidedly more flexible in that a wide variety of chloro sulfides have recently been prepared from substituted dienes.[5] Oxidation of **10** with sodium periodate in methanol at 0° afforded the desired sulfoxide in 76% yield as a colorless oil (molecular distillation, 50° (0.01 mm)).[6]

Upon heating equimolar quantities of **5** with the tetrahydrobenzindole (**6**)[4] in acetonitrile at 70° for 24 hr, a diastereomeric mixture of sulfoxides **7** as well as some rearranged amino alcohol **8b** was obtained indicating that cycloaddition and rearrangement were occurring consecutively.[8] As we have recently demonstrated, the formal transposition of sulfoxide and alcohol functions with allylic rearrangement (*i.e.*, **7** → **8b**) can be conveniently accomplished in good yields.[3a,b] Thus, on treatment of the unpurified reaction mixture from **5** and **6** with Na$_2$S·9H$_2$O in methanol for 8 hr at 65° followed by chromatography on Florisil, the desired amino alcohol **8b** was obtained as an oil which

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[1] The term cycloaddition is used here in accordance with the liberalized definition recently suggested by J. E. Baldwin, *J. Org. Chem.*, **32**, 2438 (1967).

[2] J. E. Baldwin and J. E. Patrick, *J. Amer. Chem. Soc.*, **93**, 3556 (1971), and references cited therein; P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *ibid.*, **90**, 4869 (1968), and references cited therein.

[3] (a) D. A. Evans, G. C. Andrews, and C. L. Sims, *ibid.*, **93**, 4956 (1971); (b) D. A. Evans and G. C. Andrews, *ibid.*, in press; (c) J. F. Biellmann and J. B. Ducep, *Tetrahedron Lett.*, 33 (1971); (d) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *J. Amer. Chem. Soc.*, **90**, 4758 (1968); (e) J. E. Baldwin, J. DeBernardis, and J. E. Patrick, *Tetrahedron Lett.*, 353 (1970).

[4] D. A. Evans, C. A. Bryan, and G. M. Wahl, *J. Org. Chem.*, **35**, 4122 (1970), and references cited therein.

[5] W. H. Mueller and P. G. Butler, *J. Org. Chem.*, **33**, 2642 (1968).

[6] All new compounds reported gave consistent ir, nmr, and mass spectra and combustion analyses.

[7] E. N. Prileshaeva, G. S. Vasilev, and V. H. Petrov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2217 (1967).

[8] Apparently during the reaction between **5** and **6** some **7** rearranges to **8a** and is intercepted by a nitrogen nucleophile; *cf.* D. J. Abbott and C. J. M. Stirling, *J. Chem. Soc. C*, 818 (1969).