intramolecular thermal type I ene reaction[10] of an appropriate 1,6-diene intermediate.[11,12]

To avoid loss of the stereochemical integrity by a thermal olefin migration analogous to the previously observed process **4** → **5** (Scheme II, we envisaged a suitable "protection" of the α-carboxyl group by a reduction-oxidation sequence. As a corresponding control experiment *N*-benzoylprolinol was oxidized with Jones' reagent to give *N*-benzoylproline with virtually quantitative retention of configuration. Accordingly, the carboxyl group of the carbamate **6** (Scheme III),[13] prepared from commercially available (+)-5-ethyl glutamate,[14] was reduced selectively with diborane (57% yield); subsequent silylation[15] of the resulting primary alcohol furnished the *tert*-butyldimethylsilyl ether **7**[13] (92% yield). N-Alkylation of **7** with 1-bromo-3-methyl-2-butene/NaH in HMPA[11] the monoolefin **8** (77% yield). Conversion of the saturated ester **8** to the conjugated enoate **9** caused initial difficulties since all attempts to selenate **8** employing 1 equiv of various strong bases failed completely. By contrast, deprotonation of the ester **8** using 2 equiv of lithium 2,2,6,6-tetramethylpiperidide, successive selenation of the enolate, oxidation, and selenoxide elimination[16] produced smoothly the α,β-unsaturated ester **9**[13] (48% yield). The stage was now set for the crucial closure of the five-membered ring.

Heating a 5% solution of the 1,6-diene **9** in toluene at 130 °C for 40 h using a sealed Pyrex tube gave the desired pyrrolidine **10**[13] in 75% yield. As we had anticipated, the configurations of the newly formed centers C(3) and C(4) in **10** were nicely controlled in the ene process.[17] The depicted stereochemistry agrees with the ^{1}H NMR spectrum of **10**, which exhibits two singlets at δ 4.92 and 4.71, indicating the cis relationship of the isopropenyl and ethyl acetate substituents.[18] Ultimate proof of this assignment was obtained by the conversion of the ene product **10** to (−)-α-kainic acid (**1**) as described below.

Cleavage of the silyl ether moiety of **10** by treatment with tetrabutylammonium fluoride[19] and subsequent oxidation of the resulting primary alcohol with Jones' reagent furnished the carboxylic acid **11**[13] (60% yield). Saponification of **11** with LiOH, followed by removal of the *tert*-butoxycarbonyl group with trifluoroacetic acid and subsequent treatment of an aqueous solution of the evaporated reaction mixture with in-exchange resins[11] furnished enantiomerically pure (−)-α-kainic acid (56% yield), which was then recrystallized (H_2O). ^{1}H NMR analysis of the remaining mother liquor[11] showed not even a trace of other stereoisomers, thus confirming the high stereoselectivity of the key step **9** → **10**. The synthetic (−)-α-kainic acid (mp 237–243 °C dec, $[\alpha]^{20}_D$ −15.0° (*c* 0.5, H_2O) was shown to be identical with natural **1** by mixed melting point, IR, chiroptic, and ^{1}H NMR (360 MHz) evidence. Further proof for enantiomeric purity and the identity of synthetic and natural **1** was provided by ^{1}H NMR comparison of the corresponding dimethyl ester[19] in the presence of the chiral shift reagent tris(3-(trifluoroacetyl)-*d*-camphorato)europium(III).[12]

In summary, this direct approach affords (−)-α-kainic acid from (*S*)-(+)-5-ethyl glutamate in 5% overall yield and establishes the absolute configuration of the natural products α-kainic acid (**1**), α-allokainic acid (2), and domoic acid (**3**). It furthermore illustrates the potential to achieve steric control in intramolecular ene reactions. Finally, it seems worthwhile to advance the hypothesis that in the biosynthesis of **1**–**3** (*S*)-glutamic acid and an isoprenoid unit are joined by analogous reaction schemes involving an intramolecular ene-type reaction.

Acknowledgment. Financial support of this work by the Swiss National Science Foundation, Sandoz Ltd., Basle, and Givaudan SA, Vernier, is gratefully acknowledged. We are indebted to Professor H. Morimoto for kindly providing ^{1}H NMR spectra of kainic acid stereoisomers and thank Dr. F. Gulacar for GC/MS measurements.

Registry No. 1 (R = H), 487-79-6; **6**, 82598-78-5; **7**, 82598-79-6; **8**, 82598-80-9; **9**, 82598-81-0; **10**, 82614-09-3; **11**, 82598-82-1; (+)-5-ethyl glutamate, 1119-33-1.

(10) Review: Oppolzer, W.; Snieckus, V. *Angew. Chem.* **1978**, *90*, 506; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 476. See also the diastereoselective synthesis of (±)-modhephene: Oppolzer, W.; Bättig, K. *Helv. Chim. Acta* **1981**, *64*, 2489 and ref 11 and 12.

(11) A former synthesis of racemic α-kainic acid, based on the ~70% stereoselective, thermal cyclization of the 1,5-diene **5** (Scheme II) was postulated to proceed via the transient 1,6-diene **4**: Oppolzer, W.; Andres, H. *Helv. Chim. Acta* **1979**, *62*, 2282.

(12) For a Lewis acid mediated, enantioselective ene-type cyclization leading to a synthesis of (+)-α-allokainic acid see: Oppolzer, W.; Robbiani, C.; Bättig, K. *Helv. Chim. Acta* **1980**, *63*, 2015.

(13) IR, ^{1}H NMR (360 MHz), and mass spectra are in full agreement with the assigned structure. The following compounds showed the indicated optical rotations $[\alpha]^{20}_D$ (in CH_2Cl_2): **6**, −4.2° (*c* 0.8); **7**, −22.7 (*c* 0.88); **8**, −12.0° (*c* 1.0); **9**; −3.8 (*c* 1.0); **10**, −31.8° (*c* 0.6); **11**, −63.5° (*c* 0.25).

(14) (+)-5-Ethyl glutamate (Fluka) was treated with di-*tert*-butyl dicarbonate (1.1 equiv) and NEt_3 (1.4 equiv) in DMF/H_2O (3:2), for 4 h at room temperature following the procedure described by Moroder et al. (Moroder, L.; Hallett, A.; Wünsch, E.; Keller, O.; Wersin, G. *HoppeSeyler's Z. Physiol. Chem.* **1976**, *357*, 1651) to give **6**[13] in 99% yield.

(15) Chaudhary, S. K.; Hernandez, O. *Tetrahedron Lett.* **1979**, 99.

(16) Sharpless, K. B.; Lauer, R. F.; Teranishi, A. Y. *J. Am. Chem. Soc.* **1973**, *95*, 6137. Reich, H. J.; Renga, J. M.; Reich, I. L. *Ibid.* **1975**, *97*, 5434.

(17) GC/MS analysis (capillary column, quartz, 25 m, OV 101, 200 °C) of crude as well as of chromatographed **10** indicated the presence of three isomers in a ratio of 8:83:9 (retention times 48, 49, 51 min). However, the crude primary alcohol, obtained by complete (^{1}H NMR) silyl ether cleavage of **10** (80% yield), was shown to be isomerically pure by ^{1}H NMR (100 MHz, +65 °C) as well as by resilylation, which furnished GC analytically pure **10** (60% yield). Furthermore, the subsequent conversion to (−)-kainic acid was carried out with avoidance of a possible loss of stereoisomers. It thus follows that the crucial ene reaction **9** → **10** is *at least* 83% stereoselective leading to pure (−)-kainic acid without the need to separate isomers.

(18) (a) Kondo, K.; Kondo, Y.; Takemoto, T.; Ikenoue, T. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 1899. (b) Kennewell, P. D.; Matharu, S. S.; Taylor, J. B.; Sammes, P. G. *J. Chem. Soc. Perkin Trans. 1* **1980**, 2542. (c) Oppolzer, W.; Robbiani, C. *Helv. Chim. Acta* **1980**, *63*, 2010.

(19) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.

(20) Following the procedure described in ref 3a, α-kainic acid was treated with saturated anhydrous HCl/MeOH at room temperature for 1 h to give the α-kainic acid dimethyl ester in 55% yield.

(21) **Note Added in Proof**: After completion and submission of this paper an enantioselective synthesis of (−)-domoic acid from L-glutamic acid via a Diels–Alder reaction has been described: Ohfune, Y.; Tomita, M. *J. Am. Chem. Soc.* **1982**, *104*, 3511.

19,19,19-Trifluororetinal and 20,20,20-Trifluororetinal[1]

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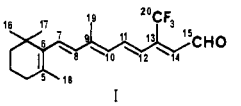
The preparation of 20,20,20-trifluororetinal (13-(trifluoromethyl)retinal), I, was reported in a recent study of the corre-



I II

sponding bacteriorhodopsin analogue.[2] We now disclose our results on the system and the related 19,19,19-trifluororetinal (II) as part of a study of fluorine-labeled visual pigments.[3] Since our work is not in agreement with the stereochemical assignment made for the reported all-*trans*-I, this communication emphasizes

(1) New geometric isomers of vitamin A and carotenoids XI. For previous paper in the series see: Miller, D.; Trammell, M.; Kini, A.; Liu, R. S. H. *Tetrahedron Lett.* **1981**, *22*, 409–412.

(2) Gärtner, W.; Oesterhelt, D.; Towner, P.; Hopf, H.; Ernst, L. *J. Am. Chem. Soc.* **1981**, *103*, 7642–7643.

(3) (a) Asato, A. E.; Matsumoto, H.; Denny, M.; Liu, R. S. H. *J. Am. Chem. Soc.* **1978**, *100*, 5957–5960. (b) Liu, R. S. H.; Matsumoto, H.; Asato, A. E.; Denny, M.; Schichida, Y.; Yoshizawa, T.; Dahlquist, F. W. *Ibid.* **1981**, *103*, 7195–7201. (c) Liu, R. S. H.; Matsumoto, H. *Methods Enzymol.* **1982**, *81*, 694–698.

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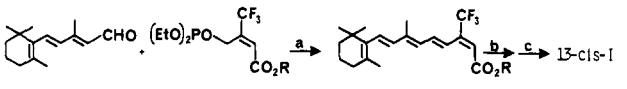
structural evidence of the synthetic intermediates as well as isomers of the fluorined retinals.

The C_5-phosphonate III, a key intermediate in the synthesis



III

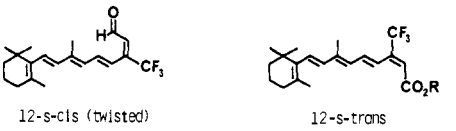
a, LDA; b, $LiAlH_4$; c, MnO_2

of I, was first reported by Pawson et al.[4] In both references,[2,4] a trans-*Z* geometry was labeled.[5] We found that III, when prepared from methyl trifluorosenecioate by NBS bromination followed by Arbuzov reaction with triethyl phosphite, gave only *cis*-III (*E*) and a 1,3-bond-shifted isomer in a ratio of 4:1. The trans-*Z* isomer of III was obtained only after photosensitized (acetophenone) isomerization of *cis*-III, producing a 2:1 (cis/trans) mixture of the two isomers. The stereochemistry of the two isomers of III was readily deduced from their NMR data.[6] Both the methylene ($\Delta\delta$ = 0.67 ppm) and the trifluoromethyl groups ($\Delta\delta$ = 5.06 ppm) exhibit expected downfield shift when cis to the carboxyl group. The extent of shifts is similar to those of isomers in a fluorinated dodeca-2,6-dienoate.[7]

Reaction of *cis*-III with the C_{15} aldehyde gave a mixture of two C_{20} esters in a ratio of 9:1. With only the exception of the CH_3-13 signal, the ^1H NMR spectra of the two compounds parallel those of the parent retinal isomers.[8] For the major isomer, the coupling constants ($J_{7,8}$ = 16, $J_{11,12}$ = 15 Hz) suggest the 7-trans and 11-trans geometry, the high-field H_8 signal (δ 6.20) the 9-trans geometry, and the low-field H_{12} (δ 7.51) the 13-cis geometry. Therefore the compound is methyl 13-*cis*-20,20,20-trifluororetinoate (all *E*).[9] It is worth noting that the CF_3 group when cis to an adjacent vinyl hydrogen provides a deshielding effect of approximately 0.5 ppm. Hence δ H_{14} for 13-*cis*-I is 6.27 while that of 13-*cis*-retinal is 5.85. The minor isomer has an unexpected 11-cis geometry ($J_{11,12}$ = 11.3 Hz). The 7-trans and 9-trans geometry are retained, as indicated by the coupling constant ($J_{7,8}$ = 16.2 Hz) and the chemical shift of H_8 (δ 6.12). The 13-cis geometry is expected to be retained in the condensation (see below). Therefore, we assigned the structure methyl 11-*cis*,13-*cis*-20,20,20-trifluororetinoate (7*E*,9*E*,11*Z*,13*E*).

Conversion of the 13-cis ester by sequential reactions with lithium aluminum hydride and manganese dioxide gave a C_{20} aldehyde in 80% yield. Since these reagents are known not to affect the stereochemistry of the polyene chain, including sterically hindered 7-cis or 11-cis isomers,[10] the aldehyde must be 13-*cis*-20,20,20-trifluororetinal (all *E*). The ^1H NMR data are almost identical with those reported for the isomer assigned the all-trans geometry.[2]

Several features in the NMR spectrum are not similar to those of the parent 13-*cis*-retinal.[8] The main one is the upfield shift of the H_{12} signal (by −0.4 ppm) resulting in an interchange of the relative chemical shifts of H_{11} and H_{12}, while in the corresponding ester H_{12} remains at lower field (see above). To rationalize the observations, we would like to suggest the existence of a sensitive variation of the 12-(*S*)-trans ⇄ 12-(*S*)-cis equi-

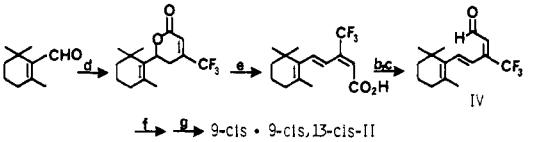


12-s-cis (twisted) 12-s-trans

librium as a result of the presence of the slightly bulkier CF_3 group. In the aldehyde the CF_3 group forces the 12,13 single bond to a twisted (*S*)-cis conformation, making H_{12} not fall in the deshielding cone of the carbonyl group; in the ester, the larger carboxyl group causes a return to the (*S*)-trans conformation with H_{12} again deshielded by the carbonyl group. Possible existence of the 12-(*S*)-cis conformer in 13-*cis*-I is supported by the recent demonstration of the presence of the 12-(*S*)-cis conformer in a substituted 13-*cis*-retinoic acid.[11]

We made two obvious, but unsuccessful, attempts to prepare all-*trans*-I. Reaction of *trans*-III with the C_{15} aldehyde was found to give the same two 13-cis isomers of the C_{20} ester. In fact, the phosphonate when recovered before completion of the reaction was found to have converted completely to *cis*-III. Hence geometric isomerization of the anion of *trans*-III must have proceeded faster than addition to the aldehyde. Also, attempt to photoisomerize 13-*cis*-I to other isomers was unsuccessful. Under normal irradiation conditions[12] the aldehyde degraded rapidly.

For the 19,19,19-trifluoro series, the CF_3 could not be introduced by reaction of β-cyclocitral with III. Instead the C_{15} acid was obtained in 30% yield via the Reformatski reaction of cyclocitral with the bromo C_5 ester, a stereospecific route giving only the 9-cis isomer.[13] After the usual reduction–oxidation sequence, the 9-*cis*-C_{15} aldehyde, IV, was obtained. The NMR data of these



d, Zn + $BrCH_2(CF_3)C{=}CHCO_2R$; e, $NaOCH_3$, CH_3OH;
f, $(EtO)_2POCH_2(CH_3)C{=}CHCN$ + LDA; g, $(i\text{-}Bu)_2AlH$

two C_{15} compounds are similar to those in I in that the downfield H_8 signal normally indicative of the 9-cis geometry[8,14] remains so only in the acid form. For the C_{15} aldehyde IV the signal for H_8 has shifted upfield by 0.79 ppm, to a region above that of H_7. This difference is again accounted for by assuming different conformations about the 8,9-bond for the aldehyde (twisted 8-(*S*)-cis) and the carboxylic acid (8-(*S*)-trans).

Reaction of IV with the cyano C_5 phosphonate gave a mixture of two C_{20} nitriles, which were converted to the aldehydes by reaction with DIBAL-*H*. The aldehydes were separated by preparative HPLC. The major isomer, a yellow solid, contained the 7-trans, 11-trans, and 13-trans geometry as indicated by the coupling constants ($J_{7,8}$ = 16.4, $J_{11,12}$ = 15.1 Hz) and the CH_3-13 (δ 2.32) H_{12} (δ 6.60), and H_{15} (δ 10.14) chemical shifts. Since the reactions are not expected to affect the 9-cis (9-*E*) geometry, the compound must be 9-*cis*-19,19,19-trifluororetinal (all *E*). The minor isomer is 9-*cis*,13-*cis*-19,19,19-trifluororetinal (7*E*,9*E*,11*E*,13*Z*): $J_{7,8}$ = 16.5 Hz; $\delta_{H\text{-}10}$ 6.65 (6.06 for that in 9-*cis*-retinal);[8a] $J_{11,12}$ = 14.5; $\delta_{CH_3\text{-}13}$ 2.14, $\delta_{H\text{-}12}$ 7.50, $\delta_{H\text{-}15}$ 10.18.

The unusual conformational properties of the polyene chain near the CF_3 group are shown in other ways. The λ_{max} in the UV absorption spectrum (hexane) of 9-*cis*-II is at 332 nm (cf. 363 for 9-*cis*-retinal[15]) and that of 9-*cis*,13-II at 330 nm (cf. 359 for 9-*cis*,13-*cis*-retinal[15]), both suggesting the presence of twisted

(4) Pawson, B. A.; Chan, K.-K., DeNoble, J.; Han, R.-J. Piermattie, V.; Specian, A. C.; Srisethnil, S.; Trown, P. W.; Bohoslawec, O.; Machlin, L. J.; Gabriel, E. *J. Med. Chem.* **1979**, *22*, 1059–1067.

(5) However, its reaction (ref 4) led to exclusively the 13-cis isomer of an aromatic retinoic acid.

(6) All NMR spectra were recorded on an IBM NR-80 spectrometer with $CDCl_3$ as solvent and C_6F_6 as internal F standard, unless otherwise specified.

(7) Camps, F.; Canela, R.; Coll, J.; Messeguer, A.; Roca, A. *Tetrahedron* **1978**, *34*, 2179–2182.

(8) (a) Patel, D. *Nature (London)* **1969**, *221*, 825–828. (b) Rowan, R.; Warshel, A.; Sykes, B. D.; Karplus, M. *Biochemistry* **1974**, *13*, 970–981. (c) Liu, R. S. H.; Asato, A. E. *Methods Enzymol.* **1982**, *88*, 506–516. (d) Kini, A.; Liu, R. S. H., unpublished results.

(9) Expectedly, the data are similar to those of 13-*cis*-20,20,20-trifluororetinoic acid recently prepared in a stereoselective synthesis: Welch, S. C.; Gruber, J. M. *J. Org. Chem.* **1982**, *47*, 385–389.

(10) (a) Asato, A. E.; Liu, R. S. H. *J. Am. Chem. Soc.* **1975**, *97*, 4128–4130. (b) Kini, A.; Matsumoto, H.; Liu, R. S. H. *Ibid.* **1979**, *101*, 5078–5079. (c) Kini, A.; Matsumoto, H.; Liu, R. S. H. *Bioorg. Chem.* **1980**, *9*, 406–410.

(11) Lewin, A. H.; Carroll, F. I.; Moreland, C. G. *J. Am. Chem. Soc.* **1981**, *103*, 6527–6529.

(12) Denny, M.; Liu, R. S. H. *J. Am. Chem. Soc.* **1977**, *99*, 4865–4867.

(13) (a) Eiter, K.; Truscheit, E.; Oediger, H. *Angew. Chem.* **1960**, *72*, 948–955. (b) Cainelli, G.; Cardillo, G. *Acc. Chem. Res.* **1981**, *14*, 89–94.

(14) Ramamurthy, V.; Tustin, G.; Yau, C. C.; Liu, R. S. H. *Tetrahedron* **1975**, *31*, 193–199.

(15) Hubbard, R.; Brown, P. K.; Bownd, D. *Methods Enzymol.* **1971**, *186*, 615–653.

chromophores. Also, in preliminary experiments, neither 13-*cis*-I, 9-*cis*-, nor 9-*cis*,13-*cis*-II gave detectable pigment analogues when incubated with a digitonin solution of cattle opsin[16]—the last two results being distinctly different from the parent retinal.[15,17] The twisted chromophores presumably no longer meet the longitudinal requirements of the binding site.[18] These results and conformational properties of I and II will be examined in detail.

Acknowledgment. The work was supported by a grant from the U.S. Public Health Services (AM 17806) and partially by the U.H. Biomedical program.

Supplementary Material Available: ^1H and ^{19}F NMR data (Figures 1–3) of 13-*cis*-I, 9-cis-II, and 9-*cis*,13-*cis*-II (4 pages). Ordering information is given on any current masthead page.

(16) Following a procedure similar to that described in Matsumoto et al. (Matsumoto, H.; Asato, A. E.; Denny, M.; Baretz, B.; Yen, Y.-P.; Tong, D.; Liu, R. S. H. *Biochemistry* **1980**, *19*, 4589–4594).
(17) Crouch, R.; Purvin, V.; Nakanishi, K.; Ebrey, T. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 1538–1542.
(18) Matsumoto, H.; Liu, R. S. H.; Simmons, C.; Seff, K. *J. Am. Chem. Soc.* **1980**, *102*, 4259–4262.

Fused Thiirene Sulfoxides. Synthesis via [2 + 4] Cycloaddition of Thiiranoradialene Sulfoxide and Structural Characterization

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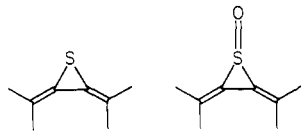
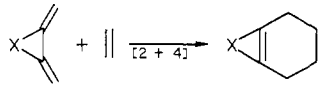
Recently we have synthesized the first hetero [3] radialenes, i.e., thiiranoradialene and its sulfoxide (**1** and **2**).[1] Although much



1 2

attention has focused on the [2 + 4] cycloaddition of radialenes with dienophiles, no examples are known for [3] radialene[2] and its analogue.[3] The addition would be synthetically useful as a means of introducing a double bond into a three-membered ring fused to a six-membered ring, thereby giving a highly strained compound (eq 1). Both **1** and **2** can be regarded as potential



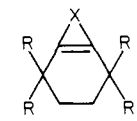
(1)

precursors for the syntheses of six-membered rings fused to thiirene and thiirene sulfoxide units, respectively.

We now report the first syntheses of alkyl-substituted thiirene sulfoxides by [2 + 4] cycloaddition of thiiranoradialene sulfoxide with 4-substituted 1,2,4-triazoline-3,5-diones (TAD) and further to demonstrate the unique structural features of the novel thiirene sulfoxide so formed.

(1) Ando, W.; Haniu, Y.; Takata, T. *Tetrahedron Lett.* **1981**, *22*, 4815–6.
(2) Kobrich, G.; Heinemann, H.; Zundorf, W. *Tetrahedron* **1967**, *23*, 565–84.
(3) Pasto, D. J.; Smorada, R. L.; Turini, B. L.; Wampfler, D. J. *J. Org. Chem.* **1976**, *41*, 432–8.

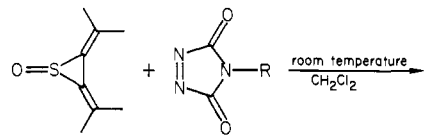
The annelated cyclopropene **3a** and cyclopropenone **3b** are the



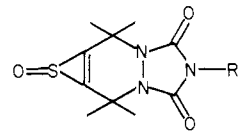
3a, X = CMe_2
b, X = C=O
c, X = C=CR_2
d, X = S
e, X = S=O

only cases reported of bicyclo[4,1,0]hept-1,6-enes.[4,5] The heteroatom analogues **3d** and **3e** as well as **3c** are unknown. Thus, it seems that the fused six-membered ring system represents the lower synthetic limits for a cyclopropene fused to a ring.

When thiiranoradialene sulfoxide **2** was treated with an equimolar amount of TAD (**4a**) in CH_2Cl_2 at room temperature (eq 2), the red color due to TAD rapidly disappeared and thiirene



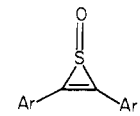
2 4a, R = Me
b, R = Ph



(2)

5a, R = Me
b, R = Ph

sulfoxide **5a** was immediately formed as colorless crystals in quantitative yield.[6] The addition proceeds equally well with phenyl-substituted TAD (**4b**) to give **5b**. However, the reaction of thiiranoradialene (**1**) with TAD gave no simple addition product but a complex product mixture, even at −50 °C,[7] although the reaction was as fast as that of **2**.[8] Apart from diaryl thiirene sulfoxide **6**,[9] thiirene sulfoxides **5a** and **5b** are the first alkyl-



6 (Ar = Ph, *p*-FPh)

substituted cases. Cycloadducts **5a** and **5b** are extraordinarily stable (104–107 °C dec) just like **6**[9] and cyclopropenone **3b** (R = Me).[5] Their structures were fully determined by elemental analyses, spectroscopies,[11] and X-ray analysis.

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(5) Suda, M.; Masamune, S. *J. Chem. Soc., Chem. Commun.* **1974**, 504–5.
(6) Attempt to prepare other [2 + 4] cycloadducts of **2** with some dienophiles such as maleic anhydride, maleinimide, ethylazodicarboxylate, etc., have failed at present time.
(7) This result may be due to the occurrence of the other reactions such as [2 + 2] cycloaddition and ene reaction, which should predominate over the [2 + 4] cycloaddition, where highly unstable thiirene can be formed.
(8) TAD, an extremely strong dienophile,[10] can react with **2** regardless of the presence of sulfoxide group (an electron-withdrawing group), because of the stabilization of the transition state.
(9) Carpino, L. A.; Chen, H.-W. *J. Am. Chem. Soc.* **1979**, *101*, 390–4.
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(11) **5a**: ^1H NMR ($CDCl_3$) δ 3.10 (s, 3 H), 1.93 (s, 6 H), 1.87 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 154.0, 153.2, 64.7, 25.1, 23.3, 22.7; IR (cm^{-1}, KBr) 2975 (w), 2925 (w), 1698 (s), 1460 (s), 1115 (s) (ν_{S-O}). Anal. Calcd for $C_{11}H_{15}N_3O_3S$: C, 49.05; H, 5.61; N, 15.60; S, 11.90. Found: C, 48.80; H, 5.56; N, 15.41; S, 12.07. **5b**: ^1H NMR ($CDCl_3$) δ 1.97 (s, 6 H), 1.90 (s, 6 H), 7.55 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 153.5, 151.4, 130.4, 128.0, 125.4, 64.8, 23.0, 22.3; IR (cm^{-1}, KBr) 3050 (w), 2950 (w), 2900 (w), 1690 (s), 1400 (s), 1115 (s) (ν_{S-O}).

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