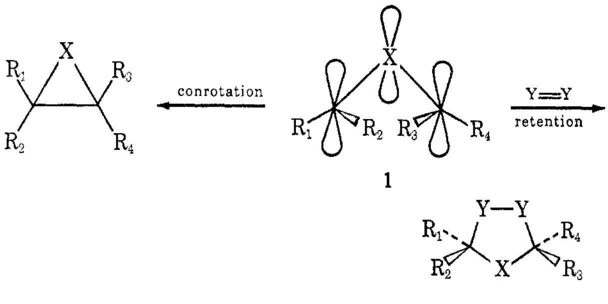
Communications

See Editorial, *J. Org. Chem.*, **37**, No. 19, 4A (1972).

Reaction of Thiocarbonyl Ylides with Diphenylketene. Stereochemistry of 1,3 Addition

Summary: *trans*-Thiocarbonyl ylides add suprafacially in a 1,3 manner over the carbonyl function of diphenylketene affording *trans*-2,4-disubstituted 5-diphenylmethylene-1,3-oxathiolanes.

Sir: The reactive intermediates **1** (X = NR, S, O), which embody an obvious potential for stereochemical labeling, have been useful in substantiating theoretical predictions made by Woodward and Hoffmann[1] for cyclization processes (eq 1). Huisgen and co-workers,[2,3] working with azomethine ylides (**1**, X = NR) first succeeded in this type of endeavor; similar demonstrations for thiocarbonyl ylides (**1**, X = S)[4] and carbonyl ylides (**1**, X = O)[5] followed.[6]



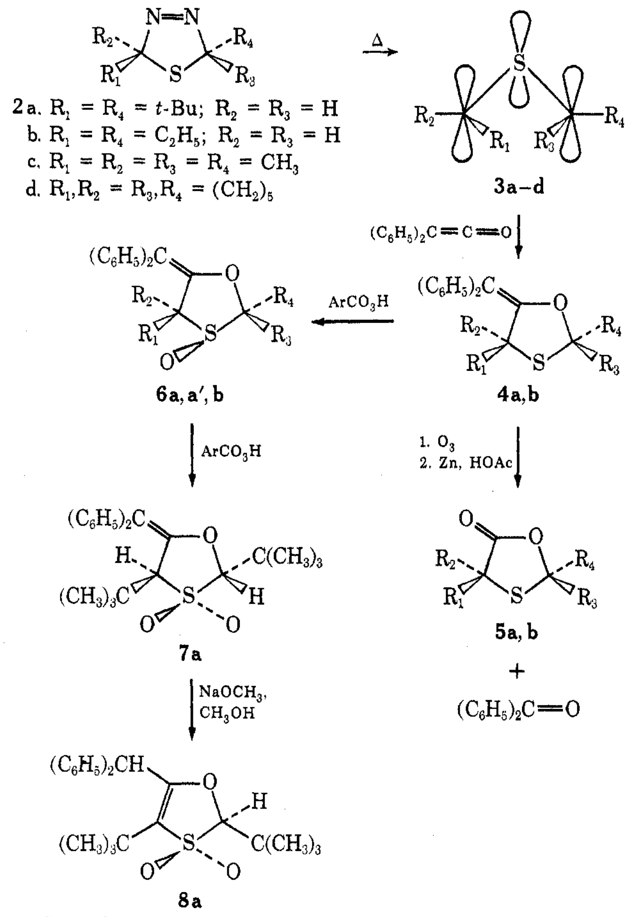
(1)

This is a report on the use of stereochemically labeled thiocarbonyl ylides to probe into the geometrical aspects of an unusual cycloaddition with diphenylketene.[7]

Pyrolysis of thiocarbonyl ylide precursors **2a,b** in hydrocarbon solvents (5 hr, 100° for **2a**, 45° for **2b**) in the presence of an equimolar amount of diphenylketene led to the formation of cycloadducts in 85–94% isolated yields (Scheme I[8]).[9] Elemental analyses and mass spectral data established that **4a,b** were 1:1 adducts of thiocarbonyl ylides **3a,b** with diphenylketene. The sharpness of the nmr spectra as well as their simplicity suggested the formation of a single isomer; no unassignable peaks were present in the nmr spectra of crude reaction mixtures before work-up. Monitoring the progress of the reaction by nmr spectroscopy failed to reveal the presence of intermediates. Lack of carbonyl absorption in **4a,b** suggested unusual, but not unprecedented,[10] 1,3 addition over the carbonyl function. The strongest evidence in favor of this structural assignment is provided by ozonization results. Cleavage of either **4a** or **4b** (ozonization of **4a** was very sluggish but clean) gave nearly quantitative yields of benzophenone and the lactones **5a,b** (ir 1770 cm^{-1}, other expected spectral features).[11]

Oxidation of **4a** with 1 equiv of *m*-chloroperbenzoic acid ($ArCO_3H$) gave two isomeric sulfoxides **6a,a′**; further oxidation of this mixture gave sulfone **7a**. A single sulfoxide, **6b**, was obtained from **4b**; the sulfone could not be obtained crystalline. The anticipated exocyclic–endocyclic shift of the double bond in **7a** took place on treatment with base. Raney

Scheme I[a]



[a] See ref 8.

---

[1] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

[2] See, for example, R. Huisgen, W. Scheer, and H. Huber, *J. Amer. Chem. Soc.*, **89**, 1753 (1967), and references compiled in ref 4c.

[3] For review and comment on these types of reactions, see (a) R. Huisgen, *Angew. Chem.*, **75**, 604 (1963); (b) R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968).

[4] (a) R. M. Kellogg and S. Wassenaar, *Tetrahedron Lett.*, 1987 (1970); (b) R. M. Kellogg, S. Wassenaar, and J. Buter, *ibid.*, 4689 (1970); (c) J. Buter, S. Wassenaar, and R. M. Kellogg, *J. Org. Chem.*, **37**, 4045 (1972).

[5] See references compiled in ref 4c.

[6] Similar demonstrations are also available for allyl anions: (a) P. Eberhard and R. Huisgen, *J. Amer. Chem. Soc.*, **94**, 1346 (1972); (b) R. Huisgen and P. Eberhard, *ibid.*, **94**, 1346 (1972); (c) G. Boche and D. Martens, *Angew. Chem.*, **84**, 768 (1972).

[7] Review of ketene chemistry: H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, N. Y., 1967, p 38.

[8] Racemic mixture; no absolute configuration implied. Stereochemical assignments for **5a,b** and **7a** made by analogy (see text).

[9] The experimental portion of this paper will appear following these pages in the microfilm edition of the Journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-73-844. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

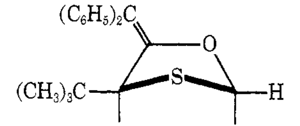
[10] (a) H. Staudinger and T. Reber, *Helv. Chim. Acta*, **4**, 3 (1921); (b) W. Kirmse, *Ber.*, **93**, 2357 (1960).

[11] See, for leading references, D. H. R. Barton and B. J. Willis, *J. Chem. Soc., Perkin Trans. 1*, 305 (1972).

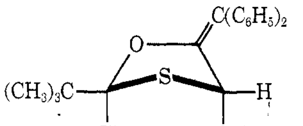
nickel desulfurization failed with highly hindered **4a**; with **4b** a mixture of products was obtained.

No characterizable products were obtained from reactions of thiocarbonyl ylide precursors **2c,d** with diphenylketene. The cis isomer of **2a**, which is only moderately stable in solution,[4c] failed to give any characterizable product besides *trans*-2,3-di-*tert*-butyl episulfide.[4c] Attempts to add **3a,b** to phenyl isocyanate failed.

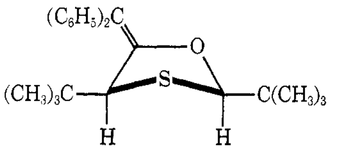
Two lines of evidence indicate that configuration has been maintained during cycloaddition; that is, *trans*-thiocarbonyl ylides **3a,b** give trans adducts **4a,b**. The most definitive arguments can be advanced for **4a**. If trans, **4a** should tend toward conformations I and II; if cis, III should approximate a preferred conformation. As anticipated, nuclear Overhauser effects (NOE) are found between the *tert*-butyl groups and the methine protons.[12] Saturation of a *tert*-butyl group at δ 0.78 results in a 24 ± 3% intensity increase of a methine proton at δ 5.11 and a 8 ± 3% increase of the other methine proton at δ 4.26. Saturation of a *tert*-butyl group at δ 0.83 results in 11 ± 3% and 24 ± 3% increases for the same two methine protons, respectively. No NOE is found between the two methine protons. These observations rhyme only with expected interactions from conformations I and II from the trans isomer of **4b**, that is, 1,3 interactions over the ring as well as interactions with the methine proton on the carbon atom to which the *tert*-butyl group is bonded. For the cis isomer of **4b** there is no obvious mechanism by which a *tert*-butyl group can cause an NOE with more than one proton, namely the proton on the carbon to which the *tert*-butyl group is bonded.[13]



I



II

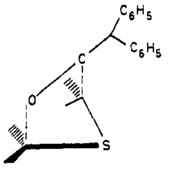


III

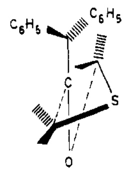
A second line of evidence is derived from the sulfoxides **6a,a′** obtained from **4a**. These are formed in about 90:10 ratio. The major isomer (**6a**), mp 175–176°, and the minor isomer (**6a′**), concentrated by repeated recovery of the mother liquors to a 60:40 mixture with **6a**, both have a single *tert*-butyl absorption shifted downfield 0.19 to 0.29 ppm relative to **4a**; in sulfone **7a** (single isomer) both *tert*-butyl groups are shifted downfield. Upfield shifts of a single methine proton also are apparent in **6a,a′**, although the effect is less clear-cut. Such behavior is not expected for the cis isomer of **4a** where shielding effects should affect either *both* methine protons or *both tert*-butyl groups.[14]

Only one isomer of sulfoxide **6b** was formed, apparently owing to a greater selectivity of oxidation of **4b**. As expected, one methine proton is shifted upfield and only one methylene group downfield consistent with trans stereochemistry.

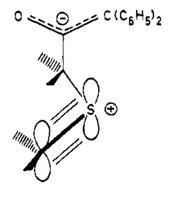
Investigations of the stereochemistry of the cycloadditions of ketenes with alkenes have revealed that the alkenic component retains configuration (reacts suprafacially) during cycloaddition,[15,16] but theory demands,[1] and stereochemical arguments are not inconsistent with,[15] *antarafacial* participation of the ketene. However, the present example is unique because, if cycloaddition is concerted and if **4a** and **4b** are truly kinetically controlled products, then in an "allowed" reaction the thiocarbonyl ylide and diphenylketene must *both* participate suprafacially $[4_s + 2_s]$ as in IV or *both* antarafacially $[4_a + 2_a]$ as in V. Providing that the foregoing "if's" are valid, then the present results indicate that IV best approximates the geometry of the transition state for cycloaddition.



IV

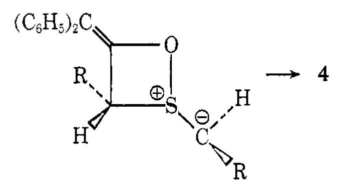


V



VI

Alternatives to the above argumentation, which presumes that there is no *a priori* electronic bias against suprafacial participation of the ketene, include the intervention of dipolar species such as VI. Also, there is precedent in sulfur diimide[17] chemistry for intermediates such as **9** (eq 2), which, if short lived under



(2)

9

---

(12) (a) J. H. Noggle and R. E. Schirmer, "The Nuclear Overhauser Effect. Chemical Applications," Wiley-Interscience, New York, N. Y., 1971; (b) G. E. Bachers and T. Schaefer, *Chem. Rev.*, **71**, 617 (1971); (c) P. D. Kennewell, *J. Chem. Educ.*, **47**, 278 (1970); (d) M. C. Woods, I. Miura, Y. Nakadaira, A. Terahara, M. Maruyamo, and K. Nakanishi, *Tetrahedron Lett.*, 321 (1967).

(13) The small separation (3 Hz) of the *tert*-butyl peaks in **4a** makes selective excitation difficult thereby raising in principle the possibility that a single *tert*-butyl group does not cause NOE's on both methine protons but rather that both *tert*-butyl groups are being excited simultaneously. However, in sulfoxide **6a**, where the *tert*-butyl groups are better separated (8 Hz), saturation of a *tert*-butyl group at δ 0.78 caused 21 ± 3% and 7 ± 3% increases in methine protons at δ 5.11 and δ 4.26, respectively. Saturation of a *tert*-butyl group at δ 0.83 resulted in 15 ± 3% and 0 ± 3% increases, respectively. Sulfoxide **6a** is likely more rigid than **4a** causing one conformation to predominate. That *tert*-butyl group in a pseudoaxial orientation produces two NOE effects, again consistent only with trans stereochemistry.

(14) Similar effects are found for *trans*-2,5-di-*tert*-butyl-2,5-dihydrothiophenes on oxidation to the sulfoxides.[4c]

(15) See, for example, (a) R. Huisgen and P. Otto, *Tetrahedron Lett.*, 4491 (1968); (b) G. Binsch, L. A. Feiler, and R. Huisgen, *ibid.*, 4497 (1968); (c) L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron*, **27**, 615 (1971); (d) R. Sustmann, A. Ansmann, and F. Vahrenholt, *J. Amer. Chem. Soc.*, **94**, 8099 (1972); (e) M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chim. Acta*, **53**, 417 (1970).

(16) Similar considerations should apply also in [2 + 6] cycloadditions for which the thus far described examples involve cyclic 6-π-electron systems also forced to react suprafacially: O. S. Rothenberger, R. T. Taylor, D. L. Dalrymple, and J. A. Moore, *J. Org. Chem.*, **37**, 2640 (1972).

(17) H. Grill and G. Kresze, *Tetrahedron Lett.*, 1427 (1970)

the reaction conditions, would escape detection. One certainly should not construe the failure to detect as proof of failure to exist.

Acknowledgment.—All NOE experiments were expertly carried out by Dr. J. de Wit of this department, to whom I am also indebted for advice.

DEPARTMENT OF ORGANIC CHEMISTRY
UNIVERSITY OF GRONINGEN
ZERNIKELAAN
GRONINGEN, THE NETHERLANDS
RICHARD M. KELLOGG

RECEIVED NOVEMBER 20, 1972

Orientation in Base-Promoted β Elimination from 2-Butyltrimethylammonium *p*-Toluenesulfonate. The Absence of a Base Association Effect

Summary: Orientation in β eliminations from 2-butyltrimethylammonium *p*-toluenesulfonate promoted by *t*-BuOK in *t*-BuOH is not influenced by base association.

Sir: Base association in solvents of low polarity, such as *t*-BuOH, has very recently been shown to profoundly affect positional and geometrical orientation[1] in base-promoted β eliminations from 2-alkyl halides and *p*-toluenesulfonates.[2,3] Investigation of a possible effect of base association upon orientation in eliminations of a charged "onium" leaving group seemed warranted.

Relative olefinic proportions from reactions of 2-butyltrimethylammonium *p*-toluenesulfonate with *t*-BuOK–*t*-BuOH are recorded in Table I. The 2-butyltrimethylammonium ion was chosen because of the absence of significant amounts of syn elimination for this substrate.[4]

TABLE I
OLEFINIC PRODUCTS FROM REACTIONS[a] OF 2-BUTYLTRIMETHYLAMMONIUM *p*-TOLUENESULFONATE[b] WITH *t*-BuOK–*t*-BuOH AT 85°

Expt	[*t*-BuOK]	% 1-butene	*trans*-2-Butene/ *cis*-2-butene
1	0.10	90.6 ± 0.5[c]	0.42 ± 0.01
2	0.25[d]	91.6 ± 0.2	0.43 ± 0.03
3	0.50	91.1 ± 0.2	0.44 ± 0.04
4	0.25[e,f]	91.7 ± 0.8	0.46 ± 0.02

[a] Ampoule technique: R. A. Bartsch, *J. Org. Chem.*, **35,** 1334 (1970). [b] [2-BuNMe$_3$OTs], 0.10 *M*. [c] Standard deviation from repetitive analysis of reaction mixture. [d] Reference 4 reports a *trans*-2-butene/*cis*-2-butene ratio of 0.42 for reaction of 2-butyltrimethylammonium iodide with 0.2–0.3 *M* *t*-BuOK–*t*-BuOH. [e] With 0.25–0.30 *M* dicyclohexyl-18-crown-6 present. [f] Average of two runs.

From the results in Table I it is clearly evident that in reactions of 2-butyltrimethylammonium ion with *t*-BuOK–*t*-BuOH positional and geometrical orientation are insensitive to changes in the base concentration (expt 1–3) or to the addition of the potassium ion complexing reagent[5] dicyclohexyl-18-crown-6[6] (expt 4). These results are in sharp contrast to those reported for eliminations from 2-butyl bromide and *p*-toluenesulfonate.[2,3] Apparently, eliminations from the 2-butyltrimethylammonium ion are being induced by *dissociated tert*-butoxide base species produced through interaction of the tetraalkylammonium salt with *t*-BuOK.[7] Base association is therefore judged to be unimportant in determining orientation for anti eliminations from "onium" compounds.

---

(1) In eliminations from a 2-substituted alkane, positional orientation refers to the relative proportions of 1- and 2-alkenes which are formed, whereas geometrical orientation compares the relative amounts of *trans*-2-alkene and *cis*-2-alkene which are produced.

(2) R. A. Bartsch, G. M. Pruss, R. L. Buswell, and B. A. Bushaw, *Tetrahedron Lett.*, 2621 (1972).

(3) R. A. Bartsch, G. M. Pruss, D. M. Cook, R. L. Buswell, B. A. Bushaw, and K. E. Wiegers, *J. Amer. Chem. Soc.*, submitted for publication.

(4) D. S. Bailey, F. C. Montgomery, G. W. Chodak, and W. H. Saunders, Jr., *ibid.*, **92**, 6911 (1970).

(5) C. J. Pederson, *ibid.*, **89**, 7017 (1967); **92**, 391 (1970).

(6) Trivial name for 2,5,8,15,18,21-hexaoxatricyclo[20.4.0.0^{9,14}]hexacosane.

(7) Benzyltrimethylammonium *tert*-butoxide is dissociated to a much greater extent than *t*-BuOK in *t*-BuOH: D. Bethell and A. F. Cockerill, *J. Chem. Soc. B*, 913 (1966).

DEPARTMENT OF CHEMISTRY
WASHINGTON STATE UNIVERSITY
PULLMAN, WASHINGTON 99163
RICHARD A. BARTSCH

RECEIVED DECEMBER 19, 1972