

benzenesulfinic acid the heat of solution was determined in 60% dioxane containing 0.34 M perchloric acid, in order to suppress any tendency for  $\text{PhSO}_2\text{H}$  to dissociate. Dissociation of benzenesulfonic acid could not be suppressed by this same procedure, and so the heat of solution of  $\text{PhSO}_3\text{H}$  itself in 60% dioxane could not be measured experimentally. Because of its rapid spontaneous hydrolysis, the heat of solution of sulfinyl sulfone 1 also could not be determined experimentally. Since cyclic sulfinyl sulfone 3 does not undergo appreciable hydrolysis in acidic 60% dioxane its heat of solution could be determined satisfactorily. Since it was found to be essentially the same ( $4.4 \pm 0.21$  kcal/mol) as that of cyclic  $\alpha$ -disulfone 4 ( $4.01 \pm 0.15$  kcal/mol), we assumed that, to an excellent approximation,  $\Delta H_{\text{soln}}$  for 1 would be the same as the measured  $\Delta H_{\text{soln}}$  for  $\alpha$ -disulfone 2.

The procedure by which either heats of solution or heats of reaction were obtained was as follows. With calorimeter, solvent, and filled ampule in place, the change in resistance,  $R$ , with time was measured (foredrift). The reaction was then activated by breaking the ampule (main experiment). A fast change in resistance was observed, followed by a slower change which was again monitored (afterdrift). The thermistor for the calorimetry system is of such a type that a decrease in temperature (endothermic process) within the calorimeter vessel results in an increase in resistance across the thermocouple. After the reaction was over (stable afterdrift), an exact amount of electrical energy (heat) was pumped into the calorimeter and the change in resistance with time was recorded (calibration run). Using a linear regression program and the data from the calibration run,  $q_{\text{calib}}$  was calculated (Hewlett-Packard 9100-A calculator, Program No. 70803). This value was then correlated with  $\Delta R$  for the main experiment to give  $q_{\text{main}}$ . Minor corrections were then made for sample buoyancy and vaporization of solvent to give  $q'_{\text{main}}$ . Dividing  $q'_{\text{main}}$  by the number of moles of substance used in the main experiment gives  $\Delta H$ . The same procedure was followed whether obtaining  $\Delta H_{\text{soln}}$  or  $\Delta H_{\text{rxn}}$ . The data for the individual runs are given in Table I. A more detailed description of the data handling procedures used is given elsewhere.<sup>13</sup>

### References and Notes

- (1) (a) This research was supported by the National Science Foundation, Grant GP 35927X. (b) Address correspondence to this author at the Department of Chemistry, Texas Tech University, Lubbock, Texas 79409.
- (2) (a) J. L. Kice and N. E. Pawlowski, *J. Am. Chem. Soc.*, **86**, 4898 (1964); (b) J. L. Kice and N. A. Favritsky, *J. Org. Chem.*, **35**, 114 (1970).
- (3) (a) J. L. Kice and G. Guaraldi, *J. Am. Chem. Soc.*, **89**, 4113 (1967); (b) J. L. Kice and L. F. Mullan, *ibid.*, **98**, 4259 (1976).
- (4) (a) J. L. Kice and G. J. Kasperek, *J. Am. Chem. Soc.*, **91**, 5510 (1969); (b) J. L. Kice, *J. Org. Chem.*, **37**, 1865 (1972); J. L. Kice and E. Legan, *J. Am. Chem. Soc.*, **95**, 3912 (1973).
- (5) (a) J. L. Kice and H. Margolis, *J. Org. Chem.*, **40**, 3623 (1975). (b) H. Margolis, Ph.D. Thesis, University of Vermont, 1976. (c) A referee has suggested that  $\Delta H_{\text{soln}}$  for 1 might be significantly different than that for 2, because 2 has a much higher melting point than 1 and could therefore have a significantly higher crystal lattice energy. However, since 4 also has a much higher melting point than 3 and yet shows virtually the same  $\Delta H_{\text{soln}}$  as 3, we personally doubt that  $\Delta H_{\text{soln}}$  for 1 differs much from that of 2.
- (6) This assumption could be subject to a few kilocalories error, but, even if it is, it is certainly not going to be large enough to change significantly the basic and important conclusion, namely, that the heat of hydrolysis of the  $\alpha$ -disulfone is substantially more exothermic than that of the sulfinyl sulfone.
- (7) (a) I. Wadso, *Acta Chem. Scand.*, **16**, 471 (1962); (b) J. B. Conn, G. B. Kistiakowsky, R. M. Roberts, and E. A. Smith, *J. Am. Chem. Soc.*, **64**, 1747 (1942).
- (8) P. George et al., *Biochim. Biophys. Acta*, **223**, 1 (1970).
- (9) G. M. Kosolapoff and H. G. Kirksey, *Dokl. Akad. Nauk. SSSR*, **176**, 1339 (1967).
- (10) J. L. Kice, D. C. Hampton, and A. Fitzgerald, *J. Org. Chem.*, **30**, 882 (1965).
- (11) U. Lerch and J. G. Moffat, *J. Org. Chem.*, **36**, 3861 (1971).
- (12) S. Sunner and I. Wadso, *Sci. Tools*, **13**, 1 (1966).
- (13) W. S. Johnson, Ph.D. Thesis, University of Vermont, 1976.

### Conversion of Triflones to Ketones

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The trifluoromethanesulfonyl group (triflyl,  $\text{CF}_3\text{SO}_2-$ ) has found extensive utility as an activating group in organic syn-

Table I. Synthesis of Ketones from Vinyl Azides

Vinyl azide	Registry no.	Ketone	Registry no.	Yield, %
	61795-22-0		451-40-1	85 <sup>a</sup>
	16717-64-9		98-86-2	93
	34910-43-5		591-78-6	86
	40934-24-5		502-49-8	91
	16719-57-6		83-33-0	87

<sup>a</sup> Yield from iodoazide.

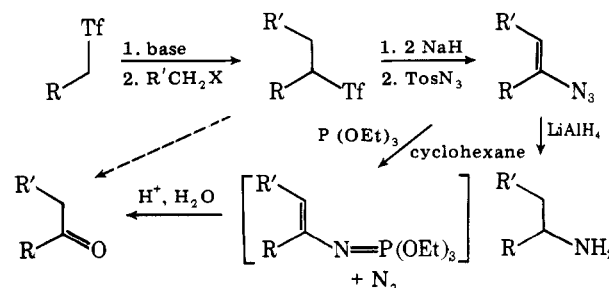
Table II. Synthesis of Ketones from Triflones

Triflone	Registry no.	Ketone	Registry no.	Yield, %
	52208-98-7			76
	62654-00-6		495-40-9	83
	62654-01-7		123-19-3	86

thesis, especially in the formation of carbon-carbon bonds.<sup>1-3</sup> One prerequisite for any such group is that after the construction step it must be easily removed or converted into other desired functionality. Previously, it was known that triflones ( $\text{C}-\text{SO}_2\text{CF}_3$ ) could be reduced to the parent alkanes or thiols, or thermally eliminated to give olefins.<sup>2</sup> In addition, it was recently shown that triflones could react with toluenesulfonyl azide in the presence of 2 equiv of base ( $\text{NaH}/\text{glyme}$ ) to give vinyl azides in good yield (Scheme I).<sup>3</sup> Reduction of these compounds with lithium aluminum hydride gave the corresponding saturated amines.

Initial attempts to hydrolyze vinyl azides to the corresponding ketones with acid were only partially successful.<sup>3</sup> In addition to ketones, amides were also produced via Schmidt rearrangement of the protonated vinyl azide.<sup>3a</sup> We reasoned that to avoid this we must first extrude the nitrogen that acts as the initiating leaving group for the rearrangement. Accordingly, we investigated the Staudinger reaction of azides with phosphines.<sup>5,6</sup> Although many kinds of azides have been studied, there appear to be few prior examples of the reaction with simple, unconjugated vinyl azides to form iminophosphoranes.<sup>7</sup>

Scheme I



The conversion of triflones to ketones was then envisioned as a "one-pot" process (Scheme I) with no intermediate purification of vinyl azide or iminophosphorane. Since the triflone-vinyl azide conversion was well established,<sup>3</sup> we first examined the reaction of vinyl azides, which can also be synthesized from olefins (via iodoazides) by treatment with iodine azide followed by base.<sup>8,9</sup> We found that treatment of vinyl azides with 1 equiv of triethyl phosphite in cyclohexane, followed directly by mild acid hydrolysis, yielded the corresponding ketones in good yield (Table I).

We then examined the direct conversion of triflones to ketones. The results obtained from these reactions, shown in Table II, reveal a very satisfactory "one-pot" operation. This conversion is particularly useful for several reasons. First, the synthesis of vinyl azides from triflones is complementary to the iodine azide method and can be used in cases when the latter method gives mixtures of ketones. With triflones the carbonyl functionality is always produced at the position originally occupied by the  $\text{CF}_3\text{SO}_2$ -group. Second, since triflones are easily obtained from readily available primary alkyl halides, and may be alkylated in high yield,<sup>2,3</sup> they represent useful synthons for the preparation of a wide variety of ketones.

### Experimental Section

**General.** Triflones,<sup>1-3</sup>  $\text{TosN}_3$ ,<sup>10</sup> and vinyl azides<sup>8,9</sup> were prepared by known methods. All compounds exhibited physical properties and give IR and NMR spectra consistent with those of known compounds.

**Synthesis of Ketones from Vinyl Azides. General Procedure.** The vinyl azide (10 mmol) was dissolved in 40 mL of dry cyclohexane. To this was added a solution of  $\text{P}(\text{OEt})_3$  (1.58 g, 9.50 mmol) in 10 mL of dry cyclohexane (addition time 10 min). The flask warmed during the addition and  $\text{N}_2$  gas was evolved. The reaction mixture was then stirred for 18–24 h and then warmed briefly to reflux. After cooling the mixture was poured into a separatory funnel and shaken intermittently for 5 min with an equal volume of 10% HCl. The two phases were then extracted with pentane ( $3 \times 50$  mL). The organic extracts were combined, washed with  $\text{H}_2\text{O}$  ( $2 \times 50$  mL) and saturated NaCl ( $2 \times 50$  mL), dried ( $\text{MgSO}_4$ ), and concentrated to give the crude ketone. The product was further purified by crystallization or distillation for comparison with authentic sample.

**Synthesis of Ketones from Triflones. General Procedure.** To a round-bottom flask was added 57% NaH-oil dispersion (926 mg, 22 mmol). The oil was removed by washing the dispersion with dry hexane ( $2 \times 10$  mL). Dry glyme [distilled from Na/benzophenone ketyl (50 mL)] was then added to the flask. To the flask was then added dropwise a solution of the triflone (10 mmol) in 10 mL of dry glyme. After 1 h the flask was cooled to  $0^\circ\text{C}$  and a solution of  $\text{TosN}_3$  (1.97 g, 10 mmol) in 10 mL of dry glyme was added dropwise over 10 min. The mixture was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was diluted with an equal volume of  $\text{Et}_2\text{O}$  and washed with  $\text{H}_2\text{O}$  ( $3 \times 100$  mL) and saturated NaCl ( $1 \times 100$  mL). The aqueous washings were combined and extracted with  $\text{Et}_2\text{O}$  ( $1 \times 100$  mL). The  $\text{Et}_2\text{O}$  washings were combined, dried ( $\text{MgSO}_4$ ), and concentrated to give the crude vinyl azide, which was suspended in 40 mL of dry cyclohexane and the treatment continued as in the procedure above.

### References and Notes

- J. B. Hendrickson, D. Sternbach, and K. Bair, *Acc. Chem. Res.*, submitted for publication, and references cited therein.
- J. B. Hendrickson, A. Giga, and J. Wareing, *J. Am. Chem. Soc.*, **96**, 2275 (1974).
- J. B. Hendrickson and P. Skipper, *Tetrahedron*, **32**, 1627 (1976).
- A. Hassner, E. Ferdinand, and R. Isbister, *J. Am. Chem. Soc.*, **92**, 1672 (1970).
- G. L'Abbé, *Ind. Chim. Belge*, **34**, 519 (1969).
- G. L'Abbé, *Angew. Chem., Int. Ed. Engl.*, **14**, 775 (1975).
- E. Ciganek, *J. Org. Chem.*, **35**, 3631 (1970). See also G. R. Harvey and K. W. Ratts, *ibid.*, **31**, 3907 (1966); G. L'Abbé and A. Hassner, *ibid.*, **36**, 258 (1971).
- F. Fowler, A. Hassner, and L. Levy, *J. Am. Chem. Soc.*, **89**, 2077 (1967).
- A. Hassner and F. Fowler, *J. Org. Chem.*, **33**, 2686 (1968).
- W. von E. Doering and C. DePuy, *J. Am. Chem. Soc.*, **75**, 5955 (1953).

### Stereospecific Cyclopentane Synthesis via Intramolecular Nitron Cycloaddition

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In 1964 LeBel and co-workers<sup>1</sup> reported an intramolecular nitron cycloaddition<sup>2</sup> in which 2,6-dimethyl-5-heptenal (melonal) was condensed with *N*-methylhydroxylamine to give a fused cyclopentane derivative. The noteworthy feature of this reaction is the fact that a cyclopentane with three contiguous asymmetric centers is stereospecifically constructed in a single step from an acyclic precursor. We wish to report further examples of this synthetic method in which functionalized cyclopentanes, again with three contiguous asymmetric centers, are prepared in good yield.

The requisite olefinic aldehyde precursors, 2-methyl-2-phenyl-5-hexenal (**3a**) and 2-(methylthio)-2-phenyl-5-hexenal (**3b**), were synthesized according to Scheme I.

2-Benzyl-4,4,6-trimethyl-5,6-dihydro-1,3(4*H*)-oxazine (1) was sequentially alkylated<sup>3</sup> with 4-bromo-1-butene and then either methyl iodide or dimethyl disulfide. Products **2a,b** were reduced with sodium borohydride and hydrolyzed with aqueous oxalic acid to afford the oily aldehydes **3a,b**. The intramolecular nitron cycloadditions were carried out by heating **3a,b** at reflux in absolute ethanol containing *N*-methylhydroxylamine hydrochloride and pyridine. Aqueous workup yielded the cycloadducts **4a,b** as oils which were converted to crystalline hydrochloride salts. The 60-MHz <sup>1</sup>H NMR spectrum of the crude free base **4a** indicated the presence of only one isomer.

Based on literature precedents,<sup>1</sup> it was anticipated that the ring juncture of **4a** would be *cis* rather than the more highly strained *trans*. This hypothesis was verified upon consideration of the 100-MHz <sup>1</sup>H NMR spectrum of **4a**·HCl (see Table I, supplementary material).

First, a long-range *W* coupling of 1 Hz is observed between  $\text{H}_{1\text{exo}}$  ( $\delta$  4.26) and  $\text{H}_{7\text{exo}}$  ( $\delta$  2.40). A reasonable *W* (i.e., approximately coplanar arms) exists between these two protons in the *cis* but not in the *trans* geometry. Secondly, the signals for the  $\text{C}_7$  protons reveal two widely different net coupling patterns with the  $\text{C}_6$  protons, an observation more consistent with the flexible *cis* structure than with the rigid *trans*.<sup>4</sup>

The assignment of the relative stereochemistry at  $\text{C}_8$  was

