Table I

Rate Data for the Solvolysis of Substituted Benzhydryl Chlorides

Substituents	Solvent, % acetone	Temp, °C	$k_1 \times 10^5$, sec^{-1}	k/k_H	$(k/k_H)_{calcd}$	$(k/k_H)_{obsd}/(k/k_H)_{calcd}$
H	80	0	0.277			
p-CH_3	80	0	7.70	27.8[a]		
p,p'-di-CH_3	80	0	~162	~585	773	~0.76[b]
H	80	25	6.07			
p-Cl	80	25	1.93	0.318[c]		
p,p'-di-Cl	80	25	0.840	0.138	0.101	1.37
p-Br	80	25	1.66	0.273[c]		
p,p'-di-Br	80	25	0.555	0.0914	0.0745	1.23
H	90	25	0.507			
p-CH_3	90	25	11.2	22.1[d]		
p,p'-di-CH_3	90	25	~143	~282	488	~0.58
p-t-C_4H_9	90	25	5.77	11.4[e]		
p,p'-di-t-C_4H_9	90	25	56.0	110	130	0.85

[a] Lit.[5] 29.6. [b] Lit.[5] 0.65. Ratios of 0.60 and 0.62 were found in the ethanolysis and 2-propanolysis, respectively.[2] [c] Values of 0.328 and 0.251 were observed in the solvolysis in 70% aqueous acetone for the p-chloro and p-bromo compounds, respectively: G. Kohnstam, *J. Chem. Soc.*, 2066 (1960). [d] Lit.[5] 20.6. [e] Lit.[5] 10.9 and 10.5 in 80% acetone at 25°.

liquid sulfur dioxide[7] and the ionization of substituted triphenylmethanols in concentrated sulfuric acid.[8,9]

Experimental Section

The known benzhydryl halides were prepared by literature procedures, and their melting points or boiling points agreed with those reported in the literature. p,p'-Di-t-butylbenzophenone was prepared from t-butylbenzene and carbon tetrachloride[10] and forms white crystals (ligroin) of mp 134.6–134.9° uncor.

Anal. Calcd for $C_{21}H_{26}O$: C, 85.66; H, 8.90. Found: C, 85.66; H, 8.89.

The 2,4-dinitrophenylhydrazone melts at 202–203°.

Anal. Calcd for $C_{27}H_{30}O_4N_4$: C, 68.33; H, 6.37. Found: C, 68.30; H, 6.02.

p,p'-Di-t-butylbenzhydrol forms white crystals (ligroin) of mp 102–102.4° uncor.

Anal. Calcd for $C_{21}H_{28}O$: C, 85.08; H, 9.52. Found: C, 85.07; H, 9.52. p,p'-Di-t-butylbenzhydryl chloride, prepared from the above with dry hydrogen chloride, was recrystallized from ligroin and had mp 122.5–123°.

Anal. Calcd for $C_{21}H_{27}Cl$: C, 80.09; H, 8.64. Found: C, 80.06; H, 8.71.

Acetone was purified by the method of Conant and Kirner.[11] The 80 and 90% acetone were prepared by adding 200 or 100 ml of distilled water to a 1-l. volumetric flask and diluting with acetone to the mark. These solvents contain slightly more acetone than the solvents used by Ingold, *et al.*,[5] who prepared them by mixing appropriate volumes of acetone and water. Solvent batches prepared for runs at different temperatures were not comparable. Rate constants were determined in the usual way by quenching 10-ml samples in 100 ml of ice-cold acetone and titrating with standard $Ba(OH)_2$. They were calculated for each point from the integrated form of the first-order rate equation. The initial concentration of chloride was determined from an infinity titer. The concentrations ranged between 0.035 and 0.04 M. Runs were usually conducted in triplicate, and rate constants within one run, as well as in duplicate runs, usually agreed within a few per cent. The rate constants for p-methylbenzhydryl chloride in 80% acetone, and those for the p,p'-dimethyl compound, in both 80 and 90% acetone, fell as the reaction progressed, those of the dimethyl compound much more than the monomethyl compound, and more in 80% than in 90% acetone.[1] Rate constants were extrapolated to 0% reaction by visually fitting the best smooth line through the points. Because of considerable scatter, the values for p,p'-dimethylbenzhydryl chloride are not very precise, but the constant in 80% acetone agrees with the constant obtained similarly by Ingold, *et al.*

Registry No.—p,p'-Di-t-butylbenzophenone, 15796-82-4; p,p'-di-t-butylbenzophenone 2,4-dinitrophenylhydrazone, 16607-59-3; p,p'-di-t-butylbenzhydrol, 16607-60-6; p,p'-di-t-butylbenzhydryl chloride, 16622-59-6.

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(7) N. C. Deno and A. Schriesheim, *J. Amer. Chem. Soc.*, **77**, 3051 (1955).

(8) N. N. Lichtin, *Progr. Phys. Org. Chem.*, **1**, 75 (1963).

(9) The argument, suggested by a referee, that the results of the solvolysis might be caused by different extents of ion pair return in mono and disubstituted benzhydryl halides, offers an alternate explanation. However, it is much less likely that this argument accounts for the results of the alcoholysis, or the data quoted at the end of the paper.

(10) The procedure was similar to that described for the preparation of benzophenone by C. S. Marvel and W. M. Sperry, "Organic Syntheses," Coll. Vol. I, 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1948, p 95.

(11) J. B. Conant and W. R. Kirner, *J. Amer. Chem. Soc.*, **46**, 232 (1924).

The Synthesis and Anionic Properties of 1,3-Dithiane 1-Oxide

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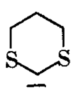
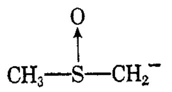
Corey and coworkers have recently developed a variety of reagents for organic synthesis utilizing the properties of sulfur (in various oxidation states) to stabilize carbanions.[2–5] The anion I derived from the title compound, 1,3-dithiane 1-oxide (II), incorporates the structural features of two of these reagents, the "dimsyl anion" (III)[2] and the dithienyl anions (IV),[3] and has been found to undergo reactions common to both.

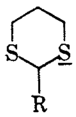


I



$CH_3—\overset{O\uparrow}{S}—CH_2^-$

III



IV

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[1] A National Science Foundation Undergraduate Summer Research Participant, 1967.

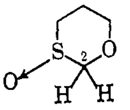
(2) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).

(3) (a) E. J. Corey and D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **4**, 1075, 1077 (1965); (b) E. J. Corey, D. Seebach, and R. Freedman, *J. Amer. Chem. Soc.*, **89**, 434 (1967); (c) E. J. Corey and D. Crouse, *J. Org. Chem.*, **33**, 298 (1968); (d) D. Seebach, N. R. Jones, and E. J. Corey, *ibid.*, **33**, 300 (1968).

(4) (a) E. J. Corey and D. Seebach, *ibid.*, **31**, 4097 (1966); (b) E. J. Corey and T. Durst, *J. Amer. Chem. Soc.*, **88**, 5656 (1966).

(5) E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1353 (1965).

1,3-Dithiane was carefully oxidized with 1 equiv of sodium metaperiodate[6] to yield (94%) a compound with the physical properties expected for 1,3-dithiane 1-oxide (II), including an interesting nuclear magnetic resonance spectrum, in which only one of the diastereomeric protons at C-2 exhibits further coupling (J_{gem} = 12 cps and J = 2.5 cps). This unusual behavior might be ascribed to conformational stability of the 1,3-dithiane 1-oxide ring, where only one proton (at lower field and presumably equatorial) is properly orientated for further coupling with a methylene proton adjacent to sulfur. Some justification for this position is found in the spectrum of another compound under investigation, 1,3-oxathiane 3-oxide (V), in which one would expect a greater amount of ring flexibility[7] and where an ABX pattern (J_{AB} = 11 cps, $J_{AX} - J_{BX}$ = 1.5 cps)[8] is observed for both the protons at position 2.



V

The optimum procedure found for rapid anion formation with minimum decomposition was to add (under nitrogen) 1 equiv of *n*-butyllithium to a cooled solution (0 to −10°) of the sulfoxide in dry tetrahydrofuran. Anion formation was rapid as evidenced by the successful reaction of the anion with benzophenone (79%) within 5 min after the final addition of *n*-butyllithium. Moreover, indications that reactions *with* the anion were also complete within minutes were found by thin layer analyses of the reaction mixtures.

1,3-Dithiane 1-oxide exhibits properties common to both sulfoxides and to dithianes in the anionic addition to benzaldehyde and benzophenone (see Chart I and Table I). Moreover, the anion can be allowed to react with ethyl benzoate to form the β-keto sulfoxide VIII (sulfoxides only) and alkylated dithianes only.[9]

CHART I

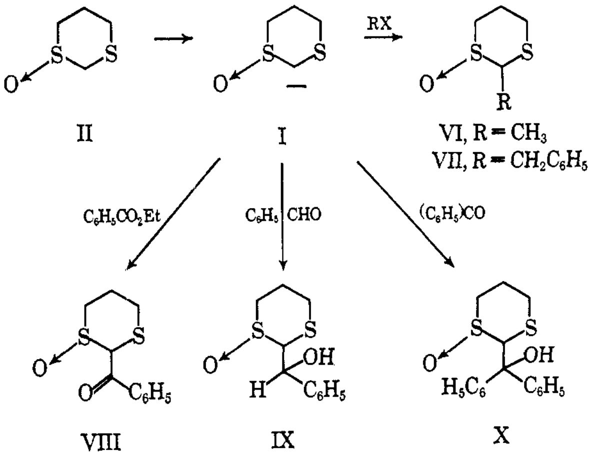


TABLE I

No.	Compound	Yield,[a] %	mp,[b] °C
II	1,3-Dithiane 1-oxide	94	87–88
VI	2-Methyl-1,3-dithiane 1-oxide	14[c]	93–94
VII	2-Benzyl-1,3-dithiane 1-oxide	24	95–96
VIII	2-Benzoyl-1,3-dithiane 1-oxide	52	134–136
IX	2-(Phenylhydroxymethyl)-1,3-dithiane 1-oxide	54	185–191 dec
X	2-(Diphenylhydroxymethyl)-1,3-dithiane 1-oxide	79	155–156 dec

[a] Yield of compound exhibiting one spot on thin layer chromatography. [b] Melting point of analytical sample. [c] Analytical sample.

The position of alkylation was confirmed to be at C-2 by comparison of the alkylated products with samples obtained by the oxidation of the corresponding methyl- or benzyl-1,3-dithiane with sodium *m*-periodate.

Like dithienyl anions (IV), the anion I possesses considerable nucleophilic character as shown by the successful benzylation with the absence of any products (*e.g.*, stilbenes) characteristic of the reaction of the "dimsyl anion" with benzyl halides.[2]

In at least one reaction, the anion I shows considerable stereoselectivity. For example, the addition product of I and benzophenone generates a second asymmetric atom at C-2, yet a single diastereomer (single spot on tlc, sharp melting point) is isolated in high yield (79%). The presence of multiple asymmetric atoms does, however, appear to present a problem with the alkylated derivatives, where the preparation of pure samples was quite difficult.

Experimental Section

Melting points were taken in capillaries, and are uncorrected. Infrared spectra were taken on a Beckman IR 10 spectrophotometer. Nmr spectra were obtained on a Varian A-60 spectrometer, with tetramethylsilane as an internal standard. The elemental analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn. The dry tetrahydrofuran was prepared shortly before use by distillation over calcium hydride.

1,3-Dithiane 1-Oxide (II).—To a cooled solution of dithiane (2.00 g, 16.7 mmol) in methanol (125 ml) was added an aqueous solution (35 ml) of sodium metaperiodate (3.68 g, 17.5 mmol) at such a rate (approximately 30 min) to maintain the temperature at 20°. Stirring and cooling were continued for an additional 30 min. The reaction mixture was then filtered to remove sodium iodate, and the resulting solution taken to near dryness on the rotary evaporator. Extraction of the solids with chloroform produced a solution which when dried over sodium sulfate, filtered, and evaporated left the crystalline sulfoxide: 2.13 g, 15.7 mmol, 94%; mp 86–87°; ir ($CHCl_3$) 1030 cm^{-1} ($S \rightarrow O$); nmr ($CDCl_3$), δ 3.84 [q, 2, $-S(\rightarrow O)CH_2S-$], 3.2 [m, 1, $-CH_2S(\rightarrow O)-$], 2.8 [m, 1, $-CH_2S(\rightarrow O)-$], 2.3 (m, 4). Two recrystallizations from chloroform–cyclohexane gave the analytical sample, mp 87–88°.

Anal. Calcd for $C_4H_8S_2O$: C, 35.26; H, 5.92; S, 47.07. Found: C, 35.40; H, 6.10; S, 47.20.

Anion Generation (General Procedure).—The flask containing a solution of 1,3-dithiane 1-oxide (0.27 g, 2.0 mmol) in dry tetrahydrofuran (8 ml) was flushed with dry nitrogen, sealed with serum caps, and placed under positive nitrogen pressure. When the stirred reaction mixture reached −10° (ice–calcium chloride), *n*-butyllithium–hexane (Alpha Inorganics Inc., 2.0 mmol) was introduced dropwise with a hypodermic syringe. As the yellow color resulting from each drop of the *n*-butyllithium solution was dispersed through the solution, 1 additional drop was added. In this manner, the temperature of the reaction mixture never exceeded −5°. The resulting solution of the carbanion was used in subsequent reactions within 5–10 min.

2-Methyl-1,3-dithiane 1-Oxide (VI).—To a solution of the carbanion prepared from 0.27 g (2.0 mmol) of the sulfoxide was added methyl iodide (0.35 g (2.5 mmol) in 3 ml of tetrahydrofuran). The solution was stirred at 0° for 30 min and then

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[6] N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

[7] F. G. Riddell, *Quart. Rev.* (London), **21**, 373 (1967).

[8] K. C. Ramsey and J. Messick [*Tetrahedron Lett.*, **49**, 4423 (1965)] find 1,3-dioxanes have couplings (C-2) of $J_{2a} - J_{2e}$ = 6.2 cps/$J_{2e} - J_{6e}$ = 1.5 cps.

[9] *For an exception, see the alkylation of β-keto* sulfoxides: G. Russell, E. Sabourin, and G. J. Mikol, *J. Org. Chem.*, **31**, 2854 (1966).

allowed to come to room temperature over a period of 60 min. The solution was evaporated and the organic products were extracted from the solid residue with chloroform. Evaporation gave a colorless oily solid. Two recrystallizations from chloroform gave analytically pure 2-methyl-1,3-dithiane 1-oxide (VI): yield 0.043 g (0.286 mmol), 14%; mp 93–94°.

Anal. Calcd for $C_5H_{10}S_2O$: C, 39.97; H, 6.71; S, 42.68. Found: C, 40.25; H, 6.89; S, 42.79.

2-Benzyl-1,3-dithiane 1-Oxide (VII).—Benzyl bromide (0.69 g, 4.05 mmol) was added to a solution of the carbanion produced from 0.500 g (3.68 mmol) of 1,3-dithiane 1-oxide (II). After stirring for an additional 4 hr, the reaction mixture was poured into water (75 ml) and acidified with hydrochloric acid. Extraction of this mixture with chloroform gave a solution that was dried over anhydrous sodium sulfate and treated with decolorizing carbon. Concentration of the solution gave an oil (0.90 g) that was purified by preparative thin layer chromatography (5% ethanol in chloroform) to give an oil that slowly crystallized: mp 51–65°; yield 0.202 g (0.888 mmol), 24%. The analytical sample (mp 95–96°) was prepared using cyclohexane–chloroform as solvent.

Anal. Calcd for $C_{11}H_{14}OS_2$: C, 58.36; H, 6.23; S, 28.33. Found: C, 58.70; H, 6.32; S, 28.50.

1-Benzoyl-1,3-dithiane 1-Oxide (VIII).—To a solution of the carbanion I produced from 1.00 g of the sulfoxide (7.36 mmol) was added ethyl benzoate (0.55 g, 3.67 mmol). After stirring for 20 min the reaction mixture was poured into water (50 ml) and carefully acidified to pH 3. Extraction with chloroform produced a yellow solution which was washed with water, dried over sodium sulfate, and filtered. The chloroform was removed to leave a yellow oil (1.01 g) that was purified *via* preparative thin layer chromatography (5% ethanol in chloroform): yield 0.45 g (1.90 mmol), 52%, off-white crystals; ir ($CHCl_3$) 1050 cm^{-1}, broad ($S\rightarrow O$), 1670 ($C{=}O$), 3430 (enol). Two recrystallizations from ethyl acetate–cyclohexane gave the analytical sample, mp 134–136°.

Anal. Calcd for $C_{11}H_{12}S_2O_2$: C, 54.96; H, 5.03; S, 26.68. Found: C, 55.21; H, 4.99; S, 26.71.

2-(Phenylhydroxymethyl)-1,3-dithiane 1-Oxide (IX).—A solution of the carbanion I in tetrahydrofuran was prepared in the usual manner from 0.50 g (3.68 mmol) of the sulfoxide. To this solution was added, over a 3-min period, a solution of benzaldehyde (0.47 g, 4.42 mmol) in tetrahydrofuran. The reaction mixture was stirred for 15 min (−5°) and the product (0.48 g, 2.0 mmol, 54%, mp 120–170°) isolated as for VII. The analytical sample (mp 185–191° dec) was prepared from chloroform–cyclohexane.

Anal. Calcd for $C_{11}H_{14}O_2S_2$: C, 54.51; H, 5.82; S, 26.46. Found: C, 54.71; H, 5.90; S, 26.21.

2-(Diphenylhydroxymethyl)-1,3-dithiane 1-Oxide (X).—To the solution of the carbanion (2.0 mmol) as prepared above was added a solution of benzophenone (0.34 g, 1.9 mmol) in dry tetrahydrofuran (2 ml). After stirring for 20 min, the product (0.49 g, 1.5 mmol, 79%, mp 158–162°) was again isolated as for VII. Several recrystallizations from chloroform–cyclohexane gave the analytical sample, mp 155–156° with decomposition.

Anal. Calcd for $C_{17}H_{18}O_2S_2$: C, 64.12; H, 5.70; S, 20.14. Found: C, 63.86; H, 5.65; S, 20.23.

1,3-Oxathiane 3-oxide (V) was prepared by the sodium metaperiodate oxidation (see preparation of II) of 1,3-oxathiane: 78%; bp 139–141° (0.6 mm); nmr ($CDCl_3$), δ 4.63 (q, 2, $-S(\rightarrow O)C\mathbf{H}_2O$), 3.85 (t, 3, $OC\mathbf{H}_2-$), 3.1 (m, 2, $-S(\rightarrow O)C\mathbf{H}_2-$), 2.0 (m, 2, $-C\mathbf{H}_2-$).

Anal. Calcd for $C_4H_8O_2S$: C, 39.98; H, 6.71; S, 26.68. Found: C, 40.01; H, 6.87; S, 26.84.

1,3-Oxathiane is a new compound[10] formed by the reaction of 3-mercapto-1-propanol with dimethoxymethane in boron trifluoride etherate–acetic acid.[11] Isolation of the crude product was effected by washing a chloroform solution of the reaction mixture several times with water and subsequent steam distillation from 10% potassium hydroxide. Vacuum distillation gave pure 1,3-oxathiane: 48%; bp 96–100° (100 mm.); nmr (pure liquid), δ 4.72 (S, 2, $SC\mathbf{H}_2O$), 3.75 (t, 2, $OC\mathbf{H}_2-$), 2.82 (t, 2, $SC\mathbf{H}_2-$), 1.8 (m, 2).

Anal. Calcd for C_4H_8OS: C, 46.12; H, 7.74; S, 30.78. Found: C, 46.43; H, 7.89; S, 30.81.

Registry No.—II, 16487-10-8; VI, 16452-25-8; VII, 16452-26-9; VIII, 16452-27-0; IX, 16452-28-1; X, 16452-29-2; V, 16452-30-5.

Acknowledgments.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Graduate School of the University of Minnesota for support of this work.

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[10] D. S. Breslow and H. Skolnik, in "Heterocyclic Compounds," Vol. 21, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1966, p 805.

[11] L. F. Fieser, *J. Amer. Chem. Soc.*, **76**, 1945 (1954).

The *syn–anti* Isomerism of α-*t*-Aminoalkanone Oximes

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The formation of α-*t*-aminoalkanone oximes in the photoaddition of N-nitrosamines to olefins led us to investigate the separation and identification of *syn* and *anti* isomers in the product (Chart I).[1] These photoadditions, as carried out under acidic conditions, usually gave exclusively or preferentially one isomer.[1-4] In cases where two geometric isomers were formed and could be isolated in the pure states, the assignment of *syn* or *anti* structures was often possible from comparison of their physical properties, although the evidence was tenuous.[3,4] Where only one isomer was isolated, however, assignment was no more than a reasonable guess since there were no general rules available.[1-4] In view of recent interest in the α-substituted (methoxy, mercapto, and halogeno groups) alkanone oximes,[5-7] it is desirable to establish a method by which *syn* and *anti* isomers can be identified rapidly. To this end, a systematic study has been carried out on the α-*t*-aminoalkanone oximes and is reported in this communication. In the sequel it is shown that compounds V and VI must possess the *anti* configuration, contrary to our original suggestion.[1,3]

The compounds examined (I–VII) were available from the previous preparative work.[1-4] The compounds of VIII series were prepared by the oximation of the appropriate α-aminoacetophenone[4] and/or by a photoaddition of the appropriate nitrosamine to styrene[3] followed by extensive chromatography. The melting points of all isomers in VIII series correspond to those prepared by different routes as reported by Fischer and Grob[8] with the exception of *anti*-VIIIc which is a new compound. These compounds can be conveniently divided into two groups; those in which

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[1] Y. L. Chow, *Can. J. Chem.*, **43**, 2711 (1965).

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[4] Y. L. Chow and C. J. Colon, *Can. J. Chem.*, **45**, 2559 (1967).

[5] R. L. Autrey and P. W. Scullard, *J. Amer. Chem. Soc.*, **87**, 3284 (1965).

[6] M. Ohno, M. Okamoto, and K. Nukada, *Tetrahedron Lett.*, 4047 (1965).

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[8] H. P. Fischer and C. A. Grob, *Helv. Chim. Acta.*, **45**, 2528 (1962).