casionally and allowed to stand at room temperature for 24 hr. After the usual work-up, the ethereal solution was concentrated and the residue was distilled to give cyclohexyl thiolisobutyrate, 7.9 g. (43%), b.p. 70–72° at 1.5 mm. Its infrared spectrum showed carbonyl absorption at 5.9 μ.

Anal. Calcd. for $C_{10}H_{18}OS$: C, 64.47; H, 9.74; S, 17.21. Found: C, 64.62; H, 9.87; S, 17.29.

Cyclohexyl Thiolpivalate.—This thiol ester was prepared by adding 11.6 g. (0.1 mole) of cyclohexyl mercaptan to a solution containing 12.1 g. (0.1 mole) of pivaloyl chloride in 100 ml. of dry pyridine at ice-bath temperature. The solution was then allowed to stand with occasional shaking at room temperature for 24 hr. After the usual work-up, distillation gave cyclohexyl thiolpivalate in 84% yield, b.p. 68° (0.6 mm.). Its infrared spectrum showed carbonyl absorption at 5.93 μ and the characteristic *t*-butyl bands at 7.19 and 7.34 μ.

Anal. Calcd. for $C_{11}H_{20}OS$: C, 65.95; H, 10.06; S, 16.00. Found: C, 66.23; H, 10.24; S, 16.29.

General Procedure For Lithium Aluminum Hydride–Boron Trifluoride Reductions.—The procedure used in the reductions of the thiol esters was identical with that of Pettit[1] using a 2:1 mole ratio of $LiAlH_4$ to thiol ester and a 15:1 mole ratio of $BF_3{\cdot}Et_2O$ to thiol ester. A solution containing both the thiol ester and $BF_3{\cdot}Et_2O$ (no diluent) was placed in a three-necked, round-bottomed flask fitted with condenser, drying tube, stirrer, and dropping funnel at ice-bath temperatures. A standard solution (*ca.* 1 *M*) of $LiAlH_4$ was then added dropwise. The mixture was allowed to stir for 45 min. The ice bath was removed and the reaction mixture was refluxed for 2 hr. Upon cooling, the mixture was hydrolyzed with 10% hydrochloric acid till two layers formed. The ether layer was separated and the aqueous layer was extracted with ether. The combined ether extracts were washed with water, saturated sodium bicarbonate solution, and saturated salt solution and then were dried over anhydrous potassium carbonate. Concentration of the ether and distillation of the residue gave the sulfide.

Cyclohexyl Ethyl Sulfide.—Cyclohexyl thiolacetate, 8 g. (0.05 mole), was reduced with $LiAlH_4$–boron trifluoride to give 5.8 g. (80%) of cyclohexyl ethyl sulfide, b.p. 74–76° (10 mm.), lit.[3] b.p. 68–70° (10 mm.), lit.[4] b.p. 72–74° (12 mm.); $n^{20}D$ 1.4885, lit.[3] 1.4908, lit.[4] 1.4890. Its infrared spectrum was identical with that of an authentic sample.[4]

Cyclohexyl Isobutyl Sulfide. A. From Cyclohexyl Thiolisobutyrate.—Cyclohexyl thiolisobutyrate, 4.65 g. (0.025 mole) was reduced with $LiAlH_4$–boron trifluoride to give 3.15 g. (73%) of cyclohexyl isobutyl sulfide, b.p. 74–76° (2.5 mm.). Its infrared spectrum was identical with an authentic sample (*vide infra*). Its nuclear magnetic resonance spectrum gave a doublet at τ 9.01 corresponding to $(CH_3)_2C$– and doublet at τ 7.67 corresponding to the methylene hydrogens neighboring the sulfur atom, *i.e.*, $-S-CH_2-C\equiv$.

Anal. Calcd. for $C_{10}H_{20}S$: C, 69.70; H, 11.70. Found: C, 69.69; H, 11.85.

B. From Cyclohexene and Isobutyl Mercaptan.—To a 100-ml., three-necked, round-bottomed flask equipped with condenser, dropping funnel, immersion thermometer, and magnetic stirrer was added 9.8 g. (0.12 mole) of cyclohexene and a few crystals of benzoyl peroxide. Isobutyl mercaptan, 9.0 g. (0.10 mole), was then added dropwise at room temperature. The reaction mixture was heated to 90° for 12 hr. Distillation of the solution gave 12 g. (70%) of cyclohexyl isobutyl sulfide, b.p. 74–76° (2.5 mm.). Its infrared spectrum was identical with that of the product obtained in the $LiAlH_4$–boron trifluoride reduction of cyclohexyl thiolisobutyrate.

Cyclohexyl Neopentyl Sulfide.—Cyclohexyl thiolpivalate, 5 g. (0.025 mole), was reduced with $LiAlH_4$–boron trifluoride. The crude material obtained before distillation showed B–H bands at 4.07 and 4.10 μ and a broad OH band at 3.13 μ indicating a boron complex. Hydrolysis of the crude material, 4.25 g., was completed by boiling at reflux for 17 hr. in 50 ml. of 10% alcoholic potassium hydroxide. The mixture was neutralized and extracted with five 50-ml. portions of ether. The combined ethereal extracts were washed with water, saturated sodium bicarbonate solution, and saturated salt solution and then were dried over anhydrous potassium carbonate. Concentration of the ether and distillation of the residue gave, in addition to a considerable still-pot residue, 1.7 g. (37%) of cyclohexyl neopentyl sulfide, b.p. 76° (0.8 mm.). Its infrared spectrum showed the usual *t*-butyl bands at 7.1 and 7.3 μ. Its nuclear magnetic resonance spectrum showed a singlet at τ 9.01 corresponding to $(CH_3)_3C$ and a singlet at τ 7.6 corresponding to the methylene hydrogens neighboring the sulfur atom, *i.e.*, $S-CH_2-C\equiv$.

Anal. Calcd. for $C_{11}H_{22}S$: C, 70.89; H, 11.90. Found: C, 71.20; H, 12.09.

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Novel Solvolytic Reactions in Dimethyl Sulfoxide

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The versatility of dimethyl sulfoxide (DMSO) as a solvent medium in organic reactions has received very widespread attention in recent years. In some cases, the ability of dimethyl sulfoxide to act as an oxidant in the course of reaction has been recognized. Kornblum and co-workers[1,2] first reported the base-catalyzed oxidation of primary tosylates and halides to aldehydes[3]; this method was extended to secondary tosylates.[4] The oxidation of ethyl bromoacetate to ethyl glyoxalate by dimethyl sulfoxide has been reported.[5] More recently, the boron fluoride-catalyzed oxidation of epoxides to α-hydroxy ketones by dimethyl sulfoxide has been described.[6]

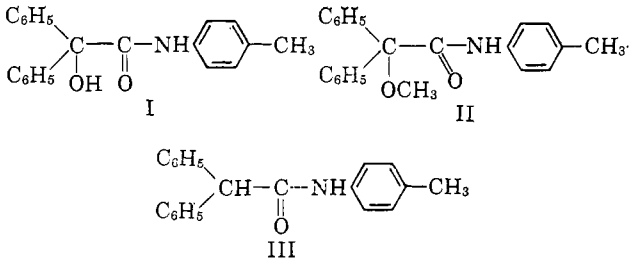
We wish herein to report the novel oxidative solvolysis of a keteneimine and a ketene in dimethyl sulfoxide under acidic conditions.

If a few drops of aqueous acid were added to a solution of diphenylketene-N-*p*-tolylimine in dimethyl sulfoxide, a high yield of N-(*p*-tolyl)-α-hydroxydiphenylacetamide (I) was obtained. Likewise, addition of diphenylketene to a dilute dimethyl sulfoxide solution of aqueous acid produced an equally high yield of benzilic acid.

If the solution of keteneimine were diluted with an excess of methanol prior to the addition of acid, N-(*p*-tolyl)-α-methoxydiphenylacetamide (II) was produced in 70% yield. This product was verified by synthesis from N-(*p*-tolyl)-α-chlorodiphenylacetamide, methanol, and triethylamine. That this product did not arise *via* etherification of the α-hydroxyamide was evident from the failure of the latter to react with methanolic hydrogen chloride. With either ketene or keteneimine, dimethyl sulfoxide, and a poor nucleophile, *i.e.*, benzoic acid, in the presence of aqueous acid, only α-hydroxy acid or α-hydroxyamide was obtained. The formation of dimethyl sulfide in this reaction was proved by converting the gas to its trimethylsulfonium salt.

(1) N. Kornblum, J. W. Powers, G. J. Anderson, W. J. Jones, H. W. Larson, O. Levand, and W. M. Weaver, *J. Am. Chem. Soc.*, **79**, 6562 (1957).
(2) N. Kornblum, W. J. Jones, and G. Anderson, *ibid.*, **81**, 4113 (1959).
(3) See also H. R. Nace and J. J. Monagle, *J. Org. Chem.*, **24**, 1792 (1959).
(4) M. M. Baizer, *ibid.*, **25**, 670 (1960).
(5) I. M. Hunsberger and J. M. Tien, *Chem. Ind.* (London), 88 (1959).
(6) T. Cohen and T. Tsuji, *J. Org. Chem.*, **26**, 1681 (1961).

When the reaction with keteneimine was carried out under rigorously anhydrous conditions, *e.g.*, dry hydrogen chloride in ether–dimethyl sulfoxide, the only product isolated was simple N-(*p*-tolyl)diphenylacetamide (III) in 66% yield. Presumably the hydrogen chloride–ketenimine adduct was formed and hydrolyzed to amide during the work-up.

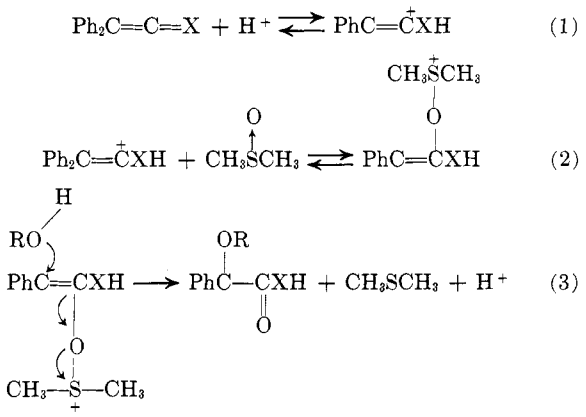


I II

III

The keteneimine was unaffected by prolonged solution in dry or slightly moist dimethyl sulfoxide alone, being recovered on dilution with water.

These results implicate dimethyl sulfoxide participation in a rapid oxidative solvolysis which appears best accomodated by the following mechanism, where =X is either =N–C$_6$H$_4$–CH$_3$ or =O.



Winstein and Smith[7] have discussed the general reactivity of dimethyl sulfoxide as a nucleophile in terms of its ability to form a sulfonium salt intermediate, R–O–$\overset{+}{S}$(CH$_3$)$_2$. The sulfonium intermediate formed in eq. 2 is entirely analogous.

The possibility of *in situ* conversion of α-diazo ketones to α-alkoxy acids as a modification of the Arndt–Eistert synthesis *via* this procedure appears attractive and is being investigated.

Experimental[8]

N-(*p*-Tolyl)-α-hydroxydiphenylacetamide.[9]—To a solution of 0.56 g. (2 mmoles) of diphenylketene-N-*p*-tolylimine[10] in 30 ml. of commercial (undried) dimethyl sulfoxide was added several drops of concentrated hydrochloric acid, and the solution was swirled. The yellow color of the keteneimine disappeared immediately; infrared inspection of petroleum ether (b.p. 30–60°) extracts showed no trace of the characteristic keteneimine band at 5 μ after admixture. After a few moments, the solution was poured into ice–water, and the resulting mixture was extracted with ether which was washed with dilute sodium bicarbonate and water, then dried, and evaporated. The solid residue was recrystallized from ethanol to yield 0.58 g. (1.8 mmoles, 91.5%) of N-(*p*-tolyl)-α-hydroxydiphenylacetamide, m.p. 189–190°, lit.[9] m.p. 189–190°; mixture melting point with authentic material was undepressed.

In one instance, the reaction was run in a flask being swept by nitrogen, and the exit gas was collected in a chilled ether trap containing an excess of methyl iodide. The ether solution was refluxed 4 hr., and the crystalline precipitate was removed. Its infrared spectrum was identical with that of authentic trimethylsulfonium iodide.

Benzilic Acid.—To a solution of several drops of concentrated hydrochloric or perchloric acid in 50 ml. of dimethyl sulfoxide was added dropwise with swirling 1.9 g. (0.01 mole) of diphenylketene. The orange ketene color was immediately discharged on contact. The solution was poured into ice–water, and the resulting precipitate was recrystallized from ethanol to yield 2.1 g. (0.0088 mole, 88%) of benzilic acid, m.p. 149–150°.

N-(*p*-Tolyl)-α-methoxydiphenylacetamide. A.—To a solution of 0.56 g. (2 mmoles) of diphenylketene-N-*p*-tolylimine in a mixture of 15 ml. of dimethyl sulfoxide and 15 ml. of methanol was added several drops of concentrated hydrochloric acid. The solution was, after a few minutes, poured into ice–water, and this was extracted with ether. The ether was washed with dilute sodium bicarbonate and water, then dried, and evaporated. The solid residue was recrystallized from ethanol to give 0.47 g. (1.4 mmoles, 71%) of N-(*p*-tolyl)-α-methoxydiphenylacetamide, m.p. 163–164°; mixture melting point with authentic material (see below) was undepressed.

N-(*p*-Tolyl)-α-methoxydiphenylacetamide. B.—To 50 ml. of dry methanol containing 5 ml. of triethylamine was added 3.3 g. (0.01 mole) of N-(*p*-tolyl)-α-chlorodiphenylacetamide,[11] and the mixture refluxed for 2 hr. The solution was diluted with ice water, and the precipitate was recrystallized from ethanol to yield 2.8 g. (0.0085 mole, 85%) of product, m.p. 163–164°. The infrared spectrum was consistent with the title structure.

Anal. Calcd. for $C_{22}H_{21}NO_2$: C, 79.75; H, 6.50. Found: C, 79.55; H, 6.40.

Reaction of Diphenylketene-N-*p*-tolylimine with Dry Hydrogen Chloride in Dimethyl Sulfoxide–Ether.—In a three-necked flask equipped with a stirrer, gas inlet, and reflux condenser and protected from moisture by a drying tube was dissolved 2.8 g. (0.01 mole) of keteneimine in a mixture of 50 ml. of dry (vacuum distilled from calcium hydride) dimethyl sulfoxide and 100 ml. of dry ether. Dry hydrogen chloride was bubbled in, while the mixture was stirred, until shortly after precipitation of dimethylsulfoxonium chloride was complete. The mixture was stirred under reflux for an additional 15 hr. The ether was decanted, washed with water, dilute sodium bicarbonate, and water, then dried, and evaporated. The residue was recrystallized from ethanol to yield 2.0 g. (0.0066 mole, 66%) of N-*p*-tolyldiphenylacetamide, m.p. 180–181°.

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(8) All melting points are uncorrected.

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(11) C. L. Stevens and J. C. French, *ibid.*, **75**, 657 (1953).

Organic Disulfides and Related Substances. VIII. Preparation and Oxidation of Some Unsymmetrical Dialkyl and Alkyl Pyridinium Disulfides[1]

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Oxidation of 2-aminoethyl disulfide dihydrochloride (1) with hydrogen peroxide afforded an excellent syn-

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