

HALOGENATED KETENES. XXX. TRIMETHYLSILYLBROMOKETENE¹

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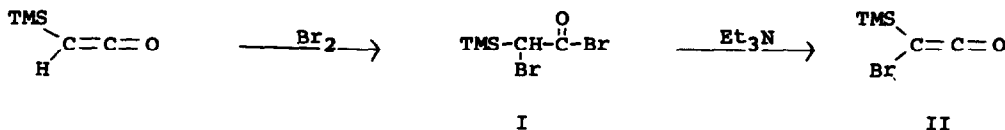
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Trimethylsilylketene has recently been reported and is remarkably stable (and yet an aldoketene, which is most unusual).² This ketene is reportedly a potent acylating agent for hindered amines and tertiary alcohols but does not undergo cycloaddition reactions with dienes and olefins.³ We wish to report the preparation of trimethylsilylbromoketene and some unusual cycloaddition reactions of this novel ketene.

Bromine readily adds to trimethylsilylketene to yield trimethylsilylbromoacetyl bromide,² (I), which will undergo triethylamine dehydrobromination to yield trimethylsilylbromoketene, (II).⁴ Thus, a 10% bromine solution in CCl₄

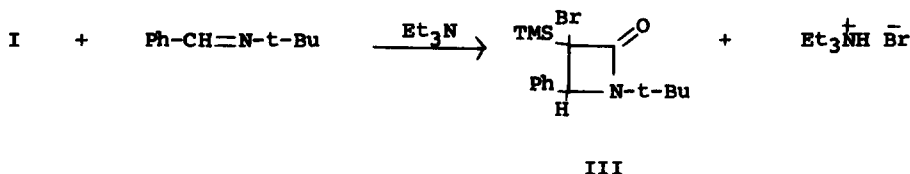


TMS = trimethylsilyl

is slowly added with stirring at room temperature to 0.01 m. of trimethylsilylketene in 75 ml. of hexane until the bromine color remained. A 0.01 m. portion

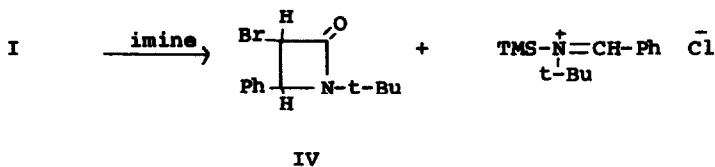
of triethylamine is then added with stirring at room temperature to produce II as evidenced by an ir band at 2114 cm^{-1} . This ketene is stable in solution even at reflux in hexane, benzene and chloroform as evidenced by the ir band. However, when the triethylammonium salt is removed from the reaction mixture, the ketene polymerizes suggesting some type of equilibrium or stabilizing influence and prohibiting isolation of the ketene. Cycloadditions of II with cyclopentadiene and vinyl ethers were unsuccessful.

Compound II undergoes cycloaddition with N-t-butylbenzylimine to produce the N-t-butyl- β -lactam, (III). Thus, to a refluxing solution of 0.01 m. of



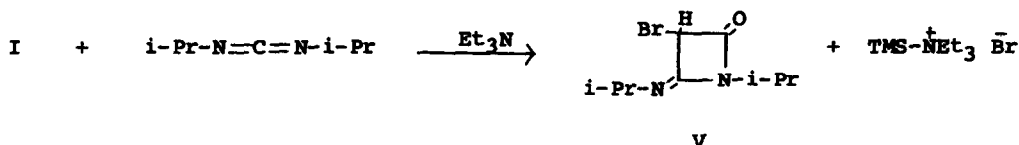
I in heptane was added 0.02 m. of the imine and then immediately 0.01 m. of triethylamine was added dropwise. After refluxing overnight, the amine salt was removed by filtration and the solvent was removed on a rotary evaporator. The residue crystallized to give a 56% yield and purification was by sublimation; mp 169° ; ir, 1733 cm^{-1} , nmr (CCl_4), δ 0.30 (s, 9 H), 1.30 (s, 9 H), 4.75 (s, 1 H) and 7.33 (s, 5 H). Mass spectrum parent peak m/e 353 and 355. Calcd. for $\text{C}_{16}\text{H}_{24}\text{BrNOSi}$: C, 54.23; H, 6.78; N, 3.95. Found: C, 54.14; H, 6.90; N, 3.90.

The absence of the triethylamine in the above preparation results in an 80% yield of the nontrimethylsilyl cycloadduct, (IV). No ketene could be de-



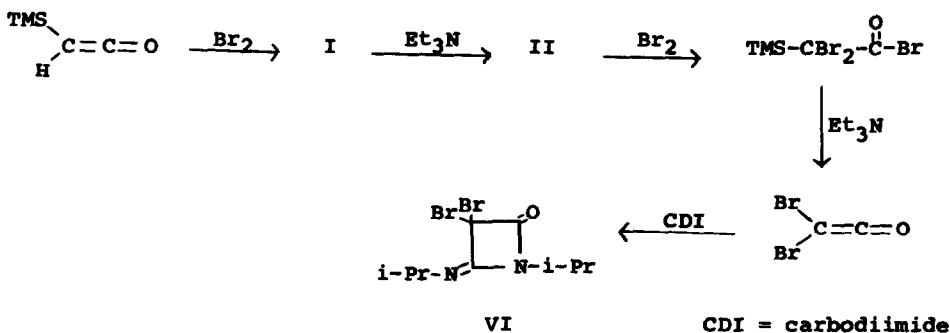
tected by ir. Apparently, the basicity of the imine is not sufficient to effect the dehydrobromination of the acid halide but does form the acylated imine salt. A second molecule of imine could then attack the silicon causing ring closure to yield the nontrimethylsilyl lactam.

The reaction of I with diisopropylcarbodiimide produced only the nontrimethylsilyl cycloadduct. (V), regardless of the presence or absence of triethyl-



amine.⁵ Thus, to a refluxing solution containing 0.01 m. of I in heptane was added 0.015 m. of diisopropylcarbodiimide followed by the immediate dropwise addition of 0.01 m. of triethylamine with stirring. After refluxing for 3 hrs., the salt was removed by filtration and the solvent evaporated. The β -lactam, V, was distilled at 72° at 0.25 mm in 90% yield; ir, 1700 and 1850 cm^{-1} ; nmr (CCl_4), δ , 1.18 (d of d 6 H), 1.38 (d, 6 H), 3.70 (m, 2 H), 4.92 (s, 1 H). Calcd. for $\text{C}_9\text{H}_{15}\text{BrN}_2\text{O}$: C, 43.72; H, 6.07; N, 11.34; Br, 32.39. Found: C, 42.13; H, 6.11; N, 11.13; Br, 35.04.

A by-product in the preparation of V was the dibromocycloadduct, VI. This



cycloadduct is due to the presence of excess bromine in the addition to trimethylsilylketene which results in some trimethylsilyldibromoacetyl bromide. This was verified by the addition of bromine to II in CCl_4 until the ir band disappeared; an equimolar amount of carbodiimide was added and at reflux, triethylamine added dropwise. After refluxing overnight, the dibromocycloadduct was obtained in 30% yield.

ACKNOWLEDGEMENTS

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2. L.L. Shchukouskaya, R.I. Pal'chik and A.N. Lazarev, Dokl. Akad. Nauk SSSR, 164, 357 (1965) as seen in Chem. Abst., 63, 18138 (1965).
3. R.A. Ruden, J. Org. Chem., 39, 3607 (1974).
4. Trimethylsilylchloroketene has also been prepared by this method.
5. Similar cycloadducts have been reported: W.T. Brady, E.D. Dorsey, and F.H. Parry, III, J. Org. Chem., 34, 2846 (1969).