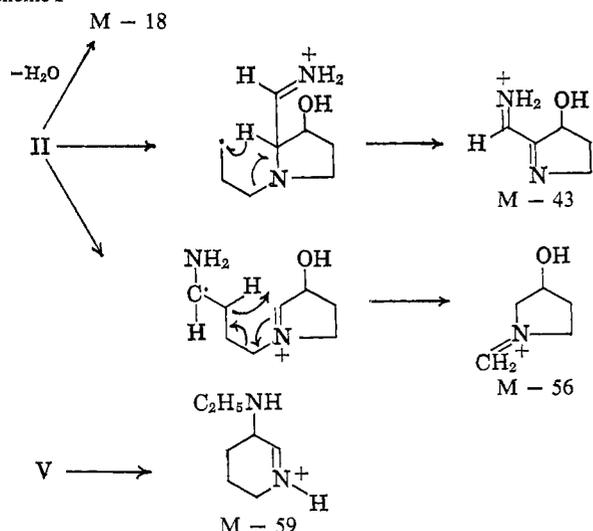


of slaframine is assigned as I, 1-acetoxy-8-aminooctahydroindolizine. The von Braun opening of the pyrrolidine ring in preference to the piperidine ring is in accord with results on known octahydroindolizines.⁹

The fragmentation pathways referred to above are summarized in Scheme I for the unacetylated compounds II and V.

Scheme I



Stereochemistry of the molecule remains to be assigned but is suggested to be that of Ia from the low frequency (1700 cm⁻¹) of the ketone formed on chromic acid oxidation of N-acetyldeacetylslaframine and the instability of slaframine free base.

Acknowledgment. This work was supported in part by Public Health Service Grant No. AI-04769 from the National Institute of Allergy and Infectious Diseases.

(9) E. Ochiai and K. Tsuda, *Ber.*, **67**, 1011 (1934).

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Cyclopropanones. III. 2,2-Dimethylcyclopropanone

Sir:

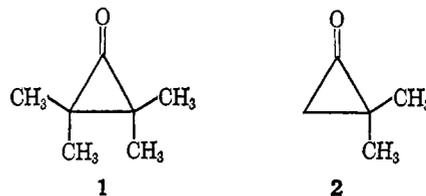
The synthesis and properties of tetramethylcyclopropanone (**1**) have been reported recently.¹⁻³ The yield of **1** as prepared by photolysis of 2,2,4,4-tetramethylcyclobutane-1,3-dione was low because of secondary photolyses. Furthermore, **1** is apparently sensitive to oxygen⁴ and its handling requires special precautions. We are therefore prompted to report a convenient, high yield synthesis and characterization of 2,2-dimethylcyclopropanone (**2**), the first example of an unsymmetrically substituted dialkylcyclopropanone.

(1) N. J. Turro and W. B. Hammond, *J. Am. Chem. Soc.*, **87**, 3258 (1965).

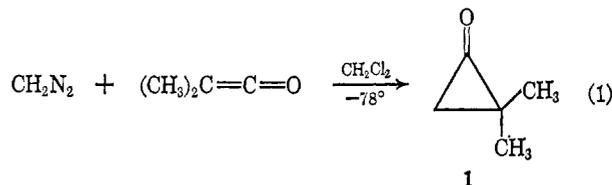
(2) N. J. Turro, W. B. Hammond, and P. A. Leermakers, *ibid.*, **87**, 2774 (1965).

(3) N. J. Turro and W. B. Hammond, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 8S.

(4) The reaction of **1** with oxygen is more complicated than originally thought² and will be reported in detail in a future publication. Attempts to prepare **1** as a pure liquid inevitably afforded dimers of **1**. The dimerization, however, may be a catalyzed process.



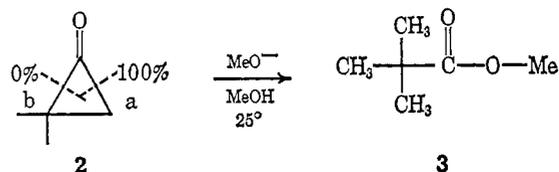
Preparation and Physical Properties of 2. Slow addition of 20 ml of a cold (-78°) methylene chloride solution of diazomethane⁵ (16 mmoles) to dimethylketene⁶ (30 mmoles in 5 ml of methylene chloride) affords **2** in >93% yield, based on diazomethane.⁷



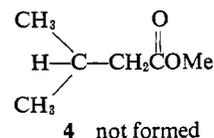
Compound **2** shows: infrared bands at $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ (cm⁻¹) 3050 (C-H stretch, cyclopropane), 1815 (C=O stretch, strained), 1380-1387 (doublet, *gem*-dimethyl group); nmr,⁸ singlets at 1.40 (two protons) and 1.20 ppm (six protons); ultraviolet spectrum, $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ 3400 Å ($\epsilon \sim 40$).

Reactions of 2. The reactions of **2** are of interest for a number of reasons including a comparison of relative reactivity with **1** and the possible effect of asymmetry of **2** in determining the direction of attack on unsymmetrical substrates.⁹

Treatment of **2** with NaOMe-MeOH leads to a >70% yield of methyl trimethylacetate (**3**). No methyl isopropylacetate (**4**) could be detected¹⁰ by vpc anal-



ysis. This result is consistent with formation of the



most stable carbanion by exclusive bond cleavage of bond a (eq 2) after attack of base on the cyclopropanone. Such a preference is predicted from results of Favorskii rearrangement of unsymmetrical α -halo ketones.¹¹

The reaction of **2** with methanol is extremely rapid¹²

(5) G. L. Closs and J. J. Coyle, *J. Am. Chem. Soc.*, **87**, 4270 (1965).

(6) W. E. Hanford and J. C. Sauer, *Org. Reactions*, **3**, 136 (1946).

(7) Vigorous evolution of nitrogen occurs even at this low temperature. The excess dimethylketene is easily separated from **2** by bulb-to-bulb distillation at $\sim 60^\circ$.

(8) All spectra reported were taken on a Varian A-60 instrument with tetramethylsilane as an external standard. Compound **1** shows a sharp singlet at 1.09 ppm in CH₂Cl₂.

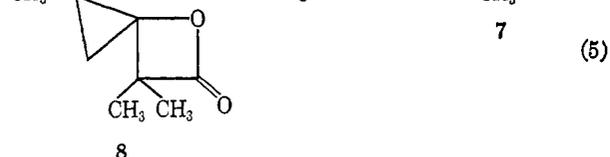
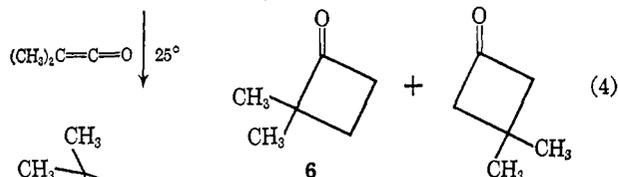
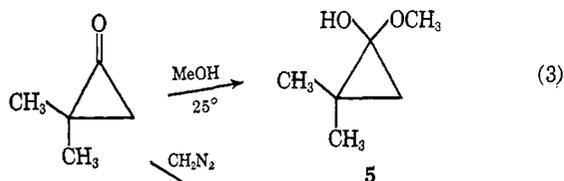
(9) The problem of interconversion of stereoisomeric cyclopropanones is also under investigation.

(10) The Favorskii rearrangement of 3-methyl-3-chloro-2-butanone and methoxide also leads to **3** as the sole rearrangement product, but in poorer yield due to *side reactions of the α -halo ketone*.¹¹

(11) For a discussion of this point see A. S. Kende, *Org. Reactions*, **11**, 261 (1960).

(12) Methanol reacts at least ten times faster with **2** than with dimethylketene.

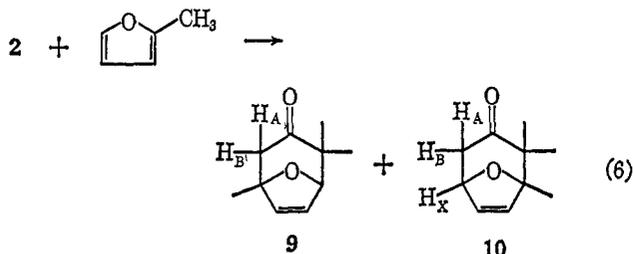
and affords the hemiketal **5** in nearly quantitative yield.¹³



Treatment of **2** with excess diazomethane (eq 4) affords the cyclobutanones **6** and **7** in the ratio 25:75, confirming earlier predictions that cyclopropanones are enormously more reactive than cyclobutanones in an uncatalyzed ring expansion with diazomethane.¹⁴⁻¹⁷

Compound **2** reacts with dimethylketene at room temperature to yield the novel cycloadduct **8** (eq 5). Compound **8** possesses the following properties: mass spectrum, m/e 154 (molecular ion, 1.1%), 110 (loss of CO_2 , 9.5%), 70 ($(\text{CH}_3)_2\text{C}=\text{C}=\text{O}$, 100%), 56 ($(\text{CH}_3)_2\text{C}^+=\text{CH}_2$, 20%); infrared, $\lambda_{\text{max}}^{\text{CCl}_4}$ 5.47 μ ; nmr AB quartet centered at 0.67 ppm ($J = 7$ cps), four three-proton singlets at 1.38, 1.29, 1.25, and 1.10 ppm.

The reaction of cyclopropanones with 1,3-dienes is predicted to occur in a concerted manner to yield 1,4-1,3 adducts.¹⁸ The addition of **2** and 2-methylfuran yields a mixture of the 1,4-1,3 adducts **9** and **10** in the ratio 58:42, a result not inconsistent with a concerted mode of addition.



Compounds **9** and **10** were shown to be isomeric by mass spectrometry (molecular ion, m/e 166 common to both); infrared of both compounds possesses $\lambda_{\text{max}}^{\text{CCl}_4}$ 1720 cm^{-1} ; nmr of **9** shows a simple AB quartet centered at 2.35 ppm ($J = 15$ cps) while **10** shows an ABX spectrum, the AB portion centered at 2.40 ppm, X centered at 4.85 ppm ($J_{\text{AB}} = 15.2$ cps, $J_{\text{AX}} = 4.7$ cps, $J_{\text{BX}} = 1.3$ cps).

(13) Compound **5** possesses molecular weight of 116 (mass spectrum) and its nmr shows an AB quartet centered at 0.58 ppm, $J = 5$ cps.

(14) J.-M. Conia and J. Salaun, *Bull. Chem. Soc. France*, 1957 (1964); M. D. Owen, G. R. Ramage, and J. E. Simonsen, *J. Chem. Soc.*, 1213 (1938).

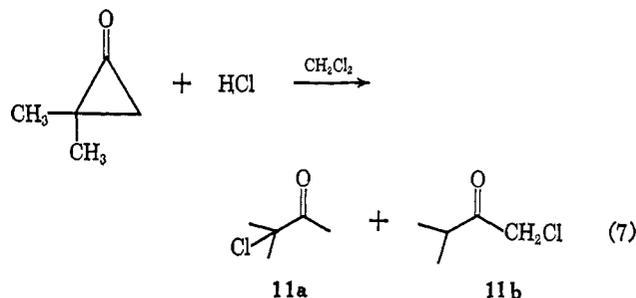
(15) P. Lipp and R. Koster, *Ber.*, **64**, 2823 (1931).

(16) D. A. Semenow, E. F. Cox, and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 3221 (1956).

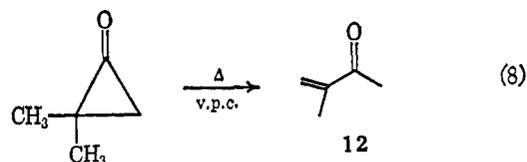
(17) A. S. Kende, Ph.D. Dissertation, Harvard University, 1956.

(18) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 4388 (1965).

Treatment of **2** with dry HCl leads to the unexpected result that the two isomeric α -chloro ketones **11a** and **11b** are produced in the rate 40:60 ($\sim 60\%$ over-all yield).



Attempts to collect **2** by preparative vpc lead to formation of methyl isopropenyl ketone (**12**).



Cyclopropanone itself is available from the reactions of diazomethane and ketene.^{15,17,19} The preparation and reactions of other cyclopropanones is under vigorous study in our laboratory.

Acknowledgments. The authors are indebted to the National Science Foundation (Grant NSF-GP-4280) and the Air Force Office of Scientific Research (Grant AFOSR-1000-66) for their generous support of this work.

(19) W. B. Hammond and N. J. Turro, unpublished results. The greater ease of handling **2** compared to **1** encourages us to feel that cyclopropanone itself may be a tractable organic compound.

(20) National Science Foundation Predoctoral Fellow, 1964-1966.

(21) Fellow of the Alfred P. Sloan Foundation.

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The Photochemical 1,3 Addition of Alcohols to Benzenes¹

Sir:

We wish to report a new photochemical reaction, the formation of alkoxy[3.1.0]bicyclohexenes by 1,3 addition of alcohols to benzene and alkylbenzenes. In the case of 1,3,5-tri-*t*-butylbenzene, the quantum yield for this addition reaction in methanol is severalfold greater than that for the isomerization observed² in hydrocarbon solutions. Furthermore, the bicyclic ether is formed to the exclusion of the isomeric hydrocarbons. The structure of the product (I) suggests that it is formed by addition³ of methanol to 1,2,4-tri-*t*-butylbenzvalene⁴ (II) or an excited state closely resembling it. It is reasonable to conclude that the same intermediate is formed in hydrocarbon solvents and is the precursor

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 4004 (1965).

(3) Related photochemical additions of alcohols to conjugated dienes are discussed by W. G. Dauben and W. T. Wipke, "Organic Photochemistry," Butterworths, London, 1965, p 539.

(4) Following the suggestion of J. Meinwald and J. K. Crandall, *J. Am. Chem. Soc.*, **88**, 1292 (1966), we are renaming benzvalene as tricyclo[3.1.0.0^{2,4}]hex-3-ene to accord with IUPAC rules. Compound III was previously² called 2,5,6-tri-*t*-butyltricyclo[2.1.0.0^{2,4}]hex-2-ene.