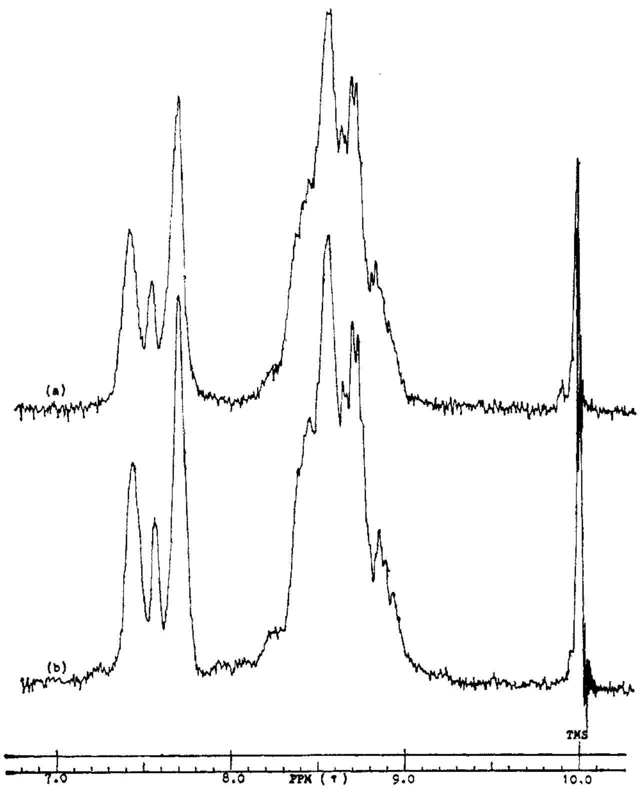

Figure 1.—(a) 60-Mc nmr spectrum of *exo*-norbornane-2-carboxylic acid from deuterioformylated norbornene. (b) 60-Mc nmr spectrum of authentic sample of 1, 30% by weight in $DCCl_3$; TMS reference.

Stoichiometric Reaction of $DCo(CO)_4$ with Norbornene.—Norbornene (2.42 g, 24.8 mmol) was dissolved in 50 ml of hexane and a small amount of some insoluble impurity was removed by filtration. About 75 ml of a hexane solution[7] of $DCo(CO)_4$ was injected in 10-ml portions over a period of 6 hr into the hexane solution of norbornene. The reaction was carried out in a serum stoppered flask connected to a gas buret, under an atmosphere of carbon monoxide and at room temperature. A total of 57.1 mmol of $DCo(CO)_4$ was used, and about 13 mmol of carbon monoxide was absorbed slowly. The reaction mixture was stirred for 24 hr, and 25 ml of dimethylformamide was added to destroy the dicobaltoctacarbonyl. About 50 ml of water was then added and the mixture was extracted with ether. The ether solution was dried with magnesium sulfate and evaporated to dryness on a rotary evaporator. The light pink viscous oil was vacuum distilled at 3 mm to give 0.65 g of clear distillate: bp 42–52°, 20% yield. The infrared spectrum of the distillate showed C-D stretching bands at 2163 and 2048 cm^{-1} and the C=O stretching band at 1713 cm^{-1}. The nmr ($DCCl_3$ solution, TMS reference) showed a multiplet from τ 7.23–7.83 (2.9 H) assigned to protons at positions 1, 2, and 4 and a multiplet from 8.08–8.97 (7.1 H) assigned to the protons at positions 3, 5, 6, and 7. An unsymmetrical doublet (J = 1 cps) at τ 0.36 due to the aldehydic proton indicated that about 7% of the product had no deuterium on the carbonyl carbon.

The aldehyde was oxidized with potassium permanganate to yield 0.13 g of the acid 1 (mp 52.0–53.5°, mmp with authentic sample, 53–54°). The nmr spectrum of the acid was taken in $DCCl_3$ (~30% by weight) and is shown in Figure 1. The carboxyl proton absorbed at τ −1.5; the carboxyl to norbornyl proton ratio was 1.0:10.0.

Registry No.—Norbornene, 498-66-8; deuterated *exo*-norbornane-2-carboxaldehyde, 20238-57-7.

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Use of N,N-Dimethylvinylamine in an Improved Synthesis of Derivatives of Thietane and Thiete[1]

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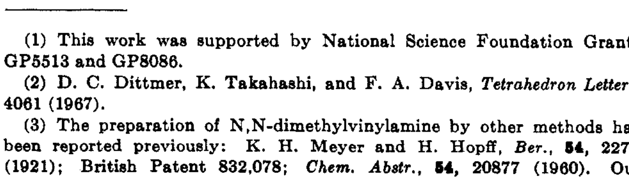
The original synthesis of thiete (thiacyclobutene) involved a long, multistep sequence starting with epichlorohydrin, and the over-all yield was relatively low.[2] Because large quantities of thiete were desired in order to study its chemical and physical properties, a new synthesis was devised utilizing the addition of "sulfene" to N,N-dimethylvinylamine, which was obtained conveniently and in high yield by dehydrohalogenation of N,N-dimethyl-N-β-chloroethylamine.[3] The addition of sulfenes to enamines is an efficient method of preparation of β-aminothietane sulfones.[4]

Both N,N-dimethyl- and N,N-diethylvinylamines were obtained by the dehydrohalogenation procedure in 84–87% yields as colorless liquids, stable below −20°. They are sensitive to air and become brown and resinous at room temperature. The nmr spectrum shows clearly the vinyl protons at τ 6.35–6.65 (CH_2=) and 3.95–4.10 (>C=C—H). The infrared spectrum shows absorption at 1630–1640 cm^{-1} attributed to the carbon–carbon double bond.

A chemical proof of the structure of N,N-dimethylvinylamine consists of its addition to sulfene to give 3-(N,N-dimethylamino)thietane 1,1-dioxide in 86% yield. The adduct can be converted either to thiete by



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(1) This work was supported by National Science Foundation Grants GP5513 and GP8086.

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procedures previously published[2,5] or to thiete 1,1-dioxide.

Experimental Section

N,N-Dimethylvinylamine.—N,N-Dimethyl-N-β-chloroethylamine hydrochloride (70.0 g, 0.485 mol) was converted to the free amine in crude form (45 g, 0.42 mol, 87%) by treatment with aqueous potassium hydroxide.[6] Pure amine can be obtained in 62% yield after distillation. The crude amine was added to a stirred solution of potassium *t*-butoxide (70.0 g, 0.625 mol) in 500 ml of purified N,N-dimethylformamide in a nitrogen atmosphere at −20°. After 15 min, the mixture was distilled (room temperature, 2 mm) until *ca.* 100 ml of liquid was collected in a receiver cooled in a bath at −78°. Fractional distillation of this liquid at 20 mm into a receiver in a bath at −78° gave N,N-dimethylvinylamine (25.0 g, 0.352 mol, 72.6% over-all).

The amine had the following properties: nmr (N,N-dimethylformamide, 60 MHz, TMS) τ 3.95 (m, =CH), 6.35–6.65 (m, =CH_2), and 7.45 ppm (s, 6 H, CH_3); ir (CCl_4) 3100 (w), 2900 (m), 1730 (w), 1690 (w), 1640 (s), 1550 (w), 1430 (m), 1335 (m), 1240 (w), 1090 (m), 1050 (w), 1000 (w), 965 (m), 940 (w), 910 (w) cm^{-1}; mass spectrum (20 eV) *m/e* 71 (parent ion), 58, 56 (parent — CH_3), 45 (parent − CH≡CH), 44, 43 (parent − $H_2C=CH_2$).

N,N-Diethylvinylamine.—By the above procedure, N,N-diethyl-N-β-chloroethylamine hydrochloride (17.2 g, 0.1 mol) was neutralized to the crude amine (11.0 g, 0.08 mol, 81%), which in turn was converted to N,N-diethylvinylamine (7.05 g, 0.071 mol, 71% overall).

This compound had the following properties: nmr (cyclohexane, 60 MHz, TMS) τ 4.10 (m, =CH), 6.30–7.60 (m 6 H, =CH_2, —CH_2—), and 8.75–9.15 ppm (2 t, 6 H, CH_3); ir (CCl_4) 2900 (s), 1720 (m), 1690 (s), 1630 (s), 1440 (s), 1370 (s), 1240 (w), 1200 (w), 1120 (s), 965 (w), 940 (w) cm^{-1}; mass spectrum (20 eV) *m/e* 99 (parent ion), 84 (parent − CH_3), 74, 73 (parent − HC≡CH), 71 (parent − $H_2C=CH_2$), 59, 58, 56, 45, 44, 31, 30.

3-(N,N-Dimethylamino)thietane 1,1-Dioxide.—Methanesulfonyl chloride (40.0 g, 0.352 mol) in 100 ml of dry ether was added dropwise to a stirred solution of pure N,N-dimethylvinylamine (25.0 g, 0.352 mol) and purified triethylamine (50.5 g, 0.500 mol) in 700 ml of dry ether at −20°. After 5 hr at −20°, triethylamine hydrochloride was removed by filtration and washed with dry ether. Ether and excess triethylamine were removed on a rotary evaporator at about 40°. The light yellow syrup obtained was recrystallized from dry ether to yield white crystals, mp 23–25° (45.5 g, 0.306 mol, 86.7%).

The adduct had the following properties: nmr (benzene, 60 MHz, TMS) τ 3.88 (2 H), 3.77 (2 H), 2.85 (1 H), and 1.95 ppm (s, 6 H, CH_3); ir (KBr) 3000 (m), 2860 (m), 2800 (m), 1460 (m), 1395 (m), 1315 (s), 1220 (s), 1175 (m), 1140 (s), 1050 (s), 975 (w), 915 (m), 850 (w), 785 (m), 765 (m), 705 (w) cm^{-1}. These spectra are identical with those of an authentic sample of 3-(N,N-dimethylamino)thietane 1,1-dioxide prepared from 3-chlorothietane 1,1-dioxide.[5a]

N,N,N-Trimethyl-N-(1,1-dioxo-3-thietanyl)ammonium Iodide.—Methyl iodide (1.5 g, 11 mmol) was added to a solution of 3-(N,N-dimethylamino)thietane 1,1-dioxide (1.49 g, 10.0 mmol) in 25 ml of methyl ethyl ketone. After 5 hr at room temperature, the white flakes of product were removed by filtration and recrystallized from 95% ethanol to yield N,N,N-trimethyl-N-(1,1-dioxo-3-thietanyl)ammonium iodide, mp 188–190° dec (lit.[5a] mp 188–190°) (2.60 g, 8.93 mmol, 89.3%) which had the following ir spectrum (KBr): 2970 (m), 2890 (m), 1460 (s), 1418 (w), 1320 (w), 1215 (s), 1140 (s), 1008 (w), 985 (w), 940 (m), 870 (w), 780 (m), 751 (w) cm^{-1}. The melting point and the infared spectrum are identical with that of the methiodide prepared from an authentic sample of 3-(N,N-dimethylamino)thietane 1,1-dioxide.[5a]

Thiete 1,1-Dioxide.—Silver oxide (1.59 g, 6.88 mmol) was mixed with N,N,N-trimethyl-N-(1,1-dioxo-3-thietanyl)ammonium iodide (1.0 g, 3.4 mmol) in 25 ml of water. The suspension was stirred for 5 min and the precipitate was removed by filtration. The aqueous filtrate was extracted three times with 25-ml portions of methylene chloride. The combined extract was dried with Drierite and evaporated to dryness on a rotary evaporator. The solids obtained were recrystallized from ether–ethanol to give thiete 1,1-dioxide (0.42 g, 2.73 mmol, 79.3%), mp 49.5–50.0° (lit.[7] mp 52–54°). When this compound was compared with an authentic sample,[7] no depression was observed in the mixture melting point, and their infrared spectra were identical.

Registry No.—N,N-Dimethylvinylamine, 5763-87-1; N,N-diethylvinylamine, 6053-97-0; 3-(N,N-dimethylamino)thietane 1,1-dioxide, 20440-18-0; N,N,N-trimethyl-N-(1,1-dioxo-3-thietanyl)ammonium iodide, 20440-19-1.

[5] (a) D. C. Dittmer and M. E. Christy, *J. Amer. Chem. Soc.*, **84**, 399 (1962); (b) D. C. Dittmer and F. A. Davis, *ibid.*, **87**, 2064 (1965).

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Synthesis and Reactions of *cis*-2,2-Dichloro-1,2,2a,7a-tetrahydro-7H-cyclobut[*a*]inden-1-one[1a]

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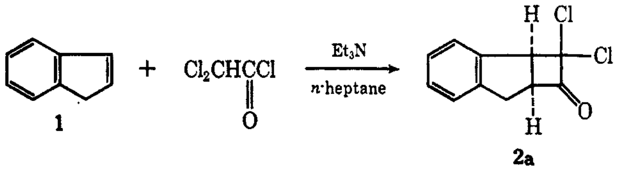
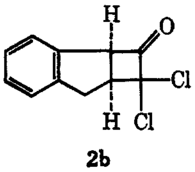
Recently, Turner and Sedan[2] reported the reaction of dichloroketene with indene to give small amounts (12%) of a compound, tentatively designated as *cis*-2,2-dichloro-1,2,2a,7a-tetrahydro-7H-cyclobut[*a*]inden-1-one, mainly on the basis of its nmr spectrum. This paper describes the synthesis and proof of structure of this compound.

The reaction of indene (1) with dichloroketene[3,4] furnished 48% yield of *cis*-2,2-dichloro-1,2,2a,7a-tetrahydro-7H-cyclobut[*a*]inden-1-one, which could have the structure **2a** or **2b**, assuming that the initial cycloaddition occurs *cis*.





2b

The compound was found to be homogenous by thin-layer and vapor-phase chromatographic analyses, and its physical constants were in agreement with those reported by the previous workers.[2] The study of nuclear magnetic resonance, infrared, and ultraviolet spectra did not prove to be of much help in distinguishing be-

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[4] L. Gosez, R. Montaigne, and P. Mollet, *Tetrahedron Lett.*, **1**, 135 (1966).