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 − $CH\equiv CH$), 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 − $HC\equiv CH$), 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).

(6) E. Baer and S. K. Pavanaram, *J. Biol. Chem.*, **236**, 2410 (1961).

(7) D. C. Dittmer and M. E. Christy, *J. Org. Chem.*, **26**, 1324 (1961).

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

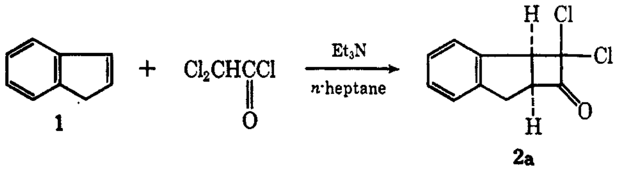
T. R. Potts and R. E. Harmon[1b]

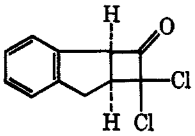
Department of Chemistry, Western Michigan University, Kalamazoo, Michigan 49001

Received February 7, 1969

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-

---

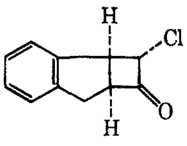
(1) (a) Robert E. Harmon and T. R. Potts, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, p 159. (b) To whom inquiries should be directed.

(2) R. W. Turner and T. Sedan, *Chem. Commun.*, **13**, 399 (1966).

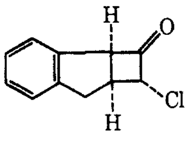
(3) H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain, and E. J. Gaugham, *J. Amer. Chem. Soc.*, **87**, 5257 (1965).

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

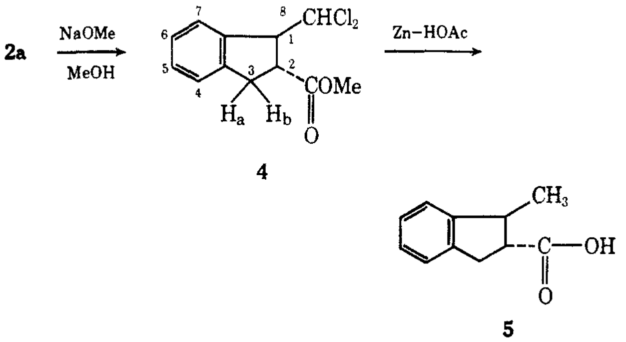
tween structures **2a** and **2b**. Catalytic hydrogenation of **2a** (or **2b**) furnished a 93% yield of 2-chloro-7H-cyclobut[*a*]inden-1-one **3a** or **3b**. Again the nuclear magnetic resonance, infrared, and ultraviolet spectra were not helpful in distinguishing between the structures **3a** and **3b**. The reaction of *cis*-2,2-dichloro-1,2,2a,7a-tetrahydro-7H-cyclobut[*a*]inden-1-one with sodium methoxide in methanol gave a 79% yield of **4** which was found to be homogenous by thin layer and vapor phase chromatographic analyses. Its ir spectrum (Nujol) showed strong absorption at 1739 cm^{-1} (—CO_2CH_3), and the nmr spectrum (CCl_4), determined on a Varian A-60 spectrometer, gave signals at τ 2.5 (m, 4, aromatics), 3.85 (d, 1, $J_{1,8}$ = 6, $CHCl_2$), 5.50 (m, 1, 1 H), 6.17 (s, 3, CO_2CH_3), and 6.53 ppm (m, 3, 2 H, 3a H and 3b H). When **4** was treated with zinc dust in acetic acid, it afforded **5** in 41% yield. Compound **5** was found to be identical with an authentic sample of *trans*-1-methyl-2-indancarboxylic acid[5] by undepressed mixture melting point and superimposable infrared spectra. The conversion of *cis*-2,2-dichloro-1,2,2a,7a-tetrahydro-7H-cyclobut[*a*]inden-1-one to *trans*-1-methyl-2-indancarboxylic acid (**5**) unequivocally proves its structure to be **2a** and not **2b**.



3a



3b



Experimental Section

The melting points were determined on a Thomas–Hoover melting point apparatus and are corrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Thin layer chromatography was done on 20 × 5 cm glass plates coated with a 0.1-mm thickness of silica gel G (Darmstadt). Vapor phase chromatographic analyses were carried out on an F & M (Model 720) instrument by using silicon gum rubber SE-30 on chromosorb P column. The infrared spectra were recorded on a Beckman IR-8 spectrophotometer. A Cary 14 spectrophotometer was used to measure the ultraviolet spectra. The nuclear magnetic resonance spectra were determined in carbon tetrachloride and deuterated chloroform as solvents and tetramethylsilane as an internal standard and were recorded on Varian A-60 and Varian HA-100 spectrometers.

cis-2,2-Dichloro-1,2,2a,7a-tetrahydro-7H-cyclobut[a]inden-1-one (2a).—A solution of 116.0 g (1.0 mol) of indene (**1**) and 74.0 g (0.74 mol) of triethylamine in 200 ml of anhydrous *n*-heptane was added dropwise with stirring to a solution of 100 g (0.68 mol) of dichloroacetyl chloride in 1 l. of anhydrous *n*-heptane. After the addition was over (*ca.* 30 min), the reaction mixture was refluxed for 15 hr. On letting it cool to 10°, triethylamine hydrochloride was precipitated. The precipitate was filtered and washed with five 200-ml portions of water. The filtrate was evaporated to dryness under reduced pressure and the resulting black oil was flash-distilled (0.1 mm). This furnished a viscous liquid which crystallized on standing to yield 64.0 g (42%) of yellowish white crystals of **2a**, mp 78–80°. It gave one spot on tlc (benzene or *p*-dioxane) and one peak on vpc. The analytical sample was obtained by one more recrystallization from petroleum ether (bp 30–60°); mp 80–81° (lit.[2] mp 78–79°); uv $\lambda_{\max}^{\mathrm{EtOH}}$ 213 (ϵ 8600) and 205 (ϵ 16,400) mμ; ir $\nu_{\max}^{\mathrm{Nujol}}$ 1821 (C=O) and 741 cm^{-1} (C—Cl).

Anal. Calcd for $C_{11}H_8Cl_2O$: C, 58.18; H, 3.55. Found: C, 58.23; H, 3.59.

2-Chloro-7H-cyclobut[a]inden-1-one (3a).—A solution of 4.0 g (0.017 mol) of **2a** in 250 ml of anhydrous *p*-dioxane was hydrogenated for 3.5 hr at room temperature and 60 psi pressure in the presence of 2.0 g of 10% palladium on carbon and 2.0 g of anhydrous calcium carbonate. The catalyst was filtered off and the filtrate was evaporated to dryness to give a white solid, which on recrystallization from petroleum ether (bp 30–60°) yielded 3.1 g (93%) of colorless crystals of **3a**, mp 111.5–112°. It gave one spot on tlc (benzene or cyclohexane) and one peak on vpc. One more recrystallization from petroleum ether furnished the analytical sample: mp 111.5–112°; uv $\lambda_{\max}^{\mathrm{EtOH}}$ 216 (ϵ 7600) and 207 mμ (ϵ 14,000); ir $\nu_{\max}^{\mathrm{Nujol}}$ 1786 (C=O) and 735 cm^{-1} (C—Cl).

Anal. Calcd for $C_{11}H_9ClO$: C, 68.58; H, 4.70; Cl, 18.41. Found: C, 68.62; H, 4.68; Cl, 18.49.

Methyl _trans_-1-(Dichloromethyl)-2-indancarboxylate (4).—To a solution of 3.0 g of sodium in 120 ml of absolute methanol at −5° was added with stirring 3.0 g (0.013 mol) of **2a**. The mixture was stirred at −5° for 30 min and then allowed to warm up to room temperature. It was neutralized with glacial acetic acid and then evaporated to dryness under reduced pressure. The resulting solid was dissolved in 50 ml of distilled water and extracted with five 150-ml portions of ether. The ether extract was dried (Na_2SO_4) and concentrated to give a yellow oil. Crystallization from petroleum ether (bp 30–60°)–ether furnished 2.7 g (79%) of colorless crystals of **4**, mp 45–46°. It gave one spot on tlc (benzene or chloroform–methanol, 20:1) and one peak on vpc; uv $\lambda_{\max}^{\mathrm{EtOH}}$ 280 (ϵ 10,400), 267 (ϵ 20,000), 236 (ϵ 19,500), and 232 mμ (ϵ 21,000); ir $\nu_{\max}^{\mathrm{Nujol}}$ 1739 (CO_2CH_3) and 741 cm^{-1} (C—Cl).

Anal. Calcd for $C_{12}H_{12}Cl_2O_2$: C, 55.61; H, 4.66; Cl, 27.36. Found: C, 55.40; H, 4.77; Cl, 27.61.

trans-1-Methylinden-2-carboxylic Acid (5).—A solution containing 50 mg (0.193 mmol) of **4** and 12.3 mg (0.193 g-atom) of powdered zinc in 25 ml of glacial acetic acid was heated under reflux for 2 hr. The reaction mixture was then cooled to room temperature and the precipitated zinc chloride was removed by filtration. The filtrate was evaporated to dryness *in vacuo*, and the resulting oil was dissolved in 10 ml of ether. The ether solution was washed with five 5-ml portions of 10% sodium bicarbonate solution, dried (Na_2SO_4), and concentrated *in vacuo* to yield 31 mg (97%) of a crude yellow oil. The oil was chromatographed over a column containing 75 g of silica gel G. Elution with 150 ml of benzene and removal of the solvent *in vacuo* gave 23 mg of a light yellow oil which was treated with 10% sodium hydroxide solution and poured into ice–water containing concentrated hydrochloric acid. On letting it stand for sometime, 13 mg (41%) of colorless crystals of **5**, mp 78–79° (lit.[5] mp 79°), was obtained; ir $\nu_{\max}^{\mathrm{Nujol}}$ 2857 (OH) and 1724 cm^{-1} (C=O). A mixture melting point with an authentic sample was undepressed.

Registry No.—**2a**, 20429-38-3; **3a**, 20429-39-4; **4**, 20429-40-7.

Acknowledgment.—This work was supported by a grant from the Michigan Cancer Foundation. The authors wish to thank Professor Don C. Iffland for help in interpreting the nmr spectra and Mr. Michael McAneny for determining the uv spectra.

---

(5) S. C. Lahiri and B. Pathak, *J. Med. Chem.*, **8**, 131 (1965).