match Sadtler No. 21402[24] and Varian Associates No. 466[25] standard spectra, respectively.

Registry No.—**1a** (2-^{14}C), 17923-95-4; **1b**, 17943-79-2; **2a** (2-^{14}C), 17923-96-5; **2b**, 503-48-0.

[24] Sadtler Standard Spectra, Sadtler Research Laboratories, Inc., Philadelphia, Pa., 1967.

[25] N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "NMR Spectra Catalog," Vol. 2, Varian Associates, 1963.

Participation of a Cyclopropane Ring in Extension of Conjugation

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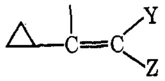
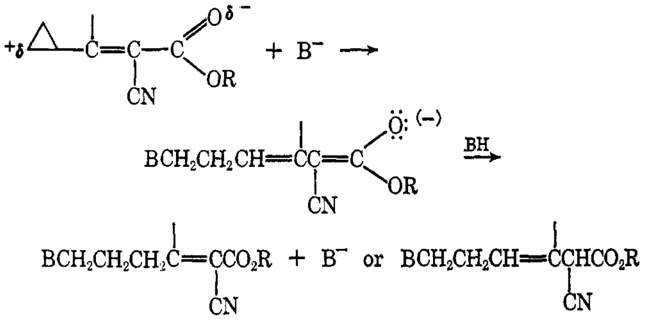
An earlier report from this laboratory[1] described ring-opening addition reactions between nucleophilic reagents and cyclopropanes which were substituted on one carbon atom of the ring by two electron-withdrawing groups.

In one simple extension of this work, the study reported here was made of the reactions of nucleophiles with structures of the type



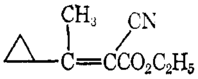
where Y and Z represent electron-withdrawing groups such as ester and nitrile. In such reactions, extension of conjugation by participation of the cyclopropane ring would result in ring-opening 1,6 addition, whereas



lack of participation by the ring would result in simple addition to the carbon–carbon double bond.

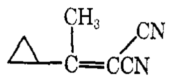
There are conflicting reports with respect to the ability of a cyclopropane ring to participate in conjugation (see typical ref 2–7, and references cited therein).

Using the method described by Cope, *et al.*,[8] for acid-catalyzed condensation of ketones with active methylene compounds, the desired starting materials, ethyl 2-cyano-3-cyclopropyl-2-butenoate (compound **1**),



1

2-cyano-3-cyclopropyl-2-butenenitrile (compound **2**),



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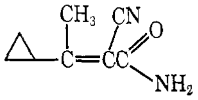
and 2-cyano-3-cyclopropyl-2-butenamide (compound **3**)

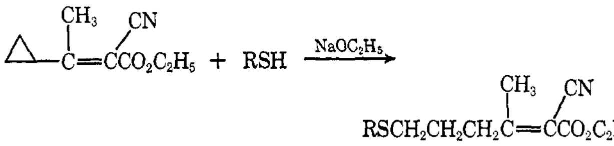


3

were prepared in good yield from methyl cyclopropyl ketone. Compound **1** was apparently a mixture of the geometrical isomers, a liquid and a crystalline solid, in approximately a 3:4 ratio. Both had the same infrared and near-infrared spectra and essentially the same elemental analysis. The liquid could be partially converted into the solid by heating at 140°. An equilibrium was apparently involved, for, if some of the solid was removed, more would form on further heating. The structure in which the methyl group is *cis* with respect to the nitrile group has been assigned to the solid isomer on the basis of nmr data. The methyl group singlet of the solid appears at the same point (δ 1.83) as observed in the spectrum of **2**, whereas in the liquid isomer this methyl group singlet appears at 1.73. The nitrile group thus apparently exerts a greater anisotropic deshielding effect than does the carboethoxy group.

Compound **3** also appeared to be a mixture of geometrical isomers. However, both were solids and separation was not so easily effected as in the case of **1**. The higher melting isomer was the major component of this mixture and was obtained pure by repeated recrystallizations. Attempts to prepare ethyl 2-carboethoxy-3-cyclopropyl-2-butenoate from methyl cyclopropyl ketone and diethyl malonate, using a variety of catalysts and reaction conditions, failed to give any of the desired product.

Reaction of **1** with benzenethiol and with 1-butanethiol in the presence of sodium ethoxide gave only one product in each case, resulting from exclusive 1,6 addition. The nmr spectra showed a complete absence of ethylenic protons in these products, indicating that the carbon–carbon double bond was entirely in a conjugated position. There were also no signals in the cyclopropyl hydrogen region of the spectra. (The complete nmr data are listed in the Experimental Section.)



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[1] J. M. Stewart and H. H. Westberg, *J. Org. Chem.*, **30**, 1951 (1965).

[2] R. C. Fuson and F. N. Baumgartner, *J. Amer. Chem. Soc.*, **70**, 3255 (1948).

[3] L. I. Smith and E. R. Rogier, *ibid.*, **73**, 3840 (1951).

[4] R. H. Eastman, *ibid.*, **76**, 4115 (1954).

[5] A. Pawda, L. Hamilton, and L. Norling *J. Org. Chem.*, **31**, 1244 (1966).

[6] W. G. Dauben and E. J. Deving, *ibid.*, **31**, 3794 (1966).

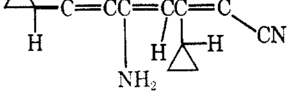
[7] T. A. Wittstruck and E. N. Trachtenberg, *J. Amer. Chem. Soc.*. **89**, 3810 (1967).

[8] A. C. Cope, C. M. Hofmann, C. Wyckoff, and E. Hardenberg, *ibid.*, **63**, 3452 (1941).

Characteristic absorption bands at 1.62–1.65 and at 2.22–2.25 μ in the near-infrared spectra have been reported by several investigators[9,10] as providing good evidence for the presence of a cyclopropane ring. In the near-infrared spectra of the addition compounds of **1** and thiols, neither of these characteristic absorption bands was present. This confirms the nmr evidence and again indicates a 1,6-addition product. In the infrared region these compounds gave a strong absorption band at 6.22 μ for the conjugated C=C group.

Reactions between various secondary amines and **1** failed to give any of the desired addition products. Short reaction times, using a solution of the reactants in ethanol in a sealed tube at 100–120°, gave mainly starting materials plus some polymer. Longer reaction times gave mainly polymers. Some of these reactions were attempted in refluxing butanol, and a new liquid compound was isolated which was the same regardless of which secondary amine was used. This compound proved to be *n*-butyl 2-cyano-3-cyclopropyl-2-butenoate, resulting from an amine-catalyzed transesterification reaction. Triethylamine failed to catalyze this exchange. Such transesterifications involving amine catalysts have been reported previously.[11]

The addition reactions of **2** were first attempted with secondary amines. Use of dimethylamine, diethylamine, and piperidine all resulted in the isolation of a single reaction product. This was a slightly yellow crystalline solid which gave the same elementary analysis as the liquid starting material. A molecular weight determination and integration of the nmr spectrum indicated that this substance was a dimer of **2**. Evidence for a possible structure for this dimer is mainly based on the ir and nmr spectra. A broad signal in the nmr spectrum at δ 5.70 with an intensity of 2 was assigned to an $-NH_2$ group, and this was confirmed by absorptions at 2.88 and 2.96 μ in the ir spectrum. A split singlet with intensity of 1 at δ 4.52 and 4.55 is believed to be due to a hydrogen attached to a carbon–carbon double bond, the splitting being due to *cis–trans* isomerism. This assignment is supported by an absorption band at 10.82 μ in the ir spectrum. The remaining 13 hydrogens all gave signals appearing as a complex multiplet between the limits of δ 0.2 and 1.66 plus one sharp singlet imposed on this multiplet at 1.23 (intensity 3). This indicates only one remaining methyl group. The compound's light yellow color and its very intense absorption in the uv spectrum centered at 323 mμ indicate a very highly conjugated system. Based on these observations and other confirming spectral evidence listed in the Experimental Section, the tentative structure



is proposed. The primary enamine grouping would be stabilized by the highly conjugated system. It is anticipated that further work will be done in an effort to elucidate further the structure of this dimer by means of chemical degradation.

Reactions of **2** with benzenethiol or 1-butanethiol in the presence of sodium ethoxide apparently gave only polymeric material.

Reactions of **3** with secondary amines failed to yield any simple addition products, and attempts to carry out base-catalyzed additions of thiols resulted only in polymers.

Experimental Section

Elemental analyses were performed by Galbraith Laboratories Knoxville, Tenn. Nuclear magnetic resonance spectra were recorded on a Varian A-60 spectrometer and on a Varian HA-60 spectrometer, using tetramethylsilane as the internal standard. Near-infrared spectra were obtained with a Hitachi Perkin-Elmer Model EPS-3T spectrophotometer, and the infrared spectra were obtained with a Beckman Model IR-5.

Condensation of Methyl Cyclopropyl Ketone[12] with Active Methylene Compounds. Preparation of 1, 2, and 3.—The condensation procedure followed the method described by Cope,[8] in which a mixture of the reactants in benzene was heated at reflux temperature in the presence of acetic acid and ammonium acetate and with a water separator.

A. Ethyl 2-Cyano-3-cyclopropyl-2-butenoate (1). Condensation with Ethyl Cyanoacetate.—After the initial reflux period of 24 hr, the solution was cooled; an equal volume of ether was added; and the solution was washed twice with water. It was then dried ($CaCl_2$) and concentrated on a steam cone, and the residue was recrystallized (70% ethanol), giving a 48% yield of the solid geometrical isomer of **1**. After six recrystallizations, this isomer melted at 81–82°: nmr ($CHCl_3$) δ 4.13 (q, 2, OCH_2CH_3), 2.22 (m, 1, cyclopropyl methine), 1.83 (s, 3, CH_3—C=C), 1.2 (t, 3, OCH_2CH_3), and 0.93 ppm (m, 4, cyclopropyl methylenes).

Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.01; H, 7.33. Found: C, 66.68; H, 7.21.

The mother liquor from the first alcohol crystallization was diluted with water; the solution was saturated with sodium chloride and was extracted twice with ether. The ethereal extract was dried ($MgSO_4$), concentrated under reduced pressure, and distilled, giving a 35% yield of the liquid isomer of **1**: bp 98–99° (0.1 mm); $n^{25}\mathrm{D}$ 1.5117; nmr signals were identical with those of the solid isomer except for a CH_3—C=C peak at 1.73 ppm.

Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.01; H, 7.33; N, 7.81. Found: C, 66.84; H, 7.37; N, 7.91.

The infrared spectra of the isomers were identical in most details and included $\lambda_{\max}^{\mathrm{CCl_4}}$ 4.50 (w, C≡N), 5.80 (vs, ester C=O), and 6.32 (s, conjd C=C) μ. The near-infrared spectra showed the definitive cyclopropane C–H absorptions: $\lambda_{\max}^{\mathrm{CCl_4}}$ 1.635 (w) and 2.220 (s) μ.

B. 2-Cyano-3-cyclopropyl-2-butenenitrile (2). Condensation with Malononitrile.—Following the reflux period, the initial crude product was isolated as described for **1** above. Recrystallization (70% ethanol) gave an 88% yield of **2**, after three recrystallizations: mp 65.0–66°; $\lambda_{\max}^{\mathrm{CCl_4}}$ 4.46 (s, C≡N), 6.36 (s, conjd C=C) μ; near-ir (CCl_4) 1.627 (m) and 2.222 μ (s, cyclopropyl); nmr ($CHCl_3$) δ 2.25 (m, 1, cyclopropyl methine), 1.83 (s, 3, CH_3—C=C), and 1.15 ppm (m, 4, cyclopropyl methylenes).

Anal. Calcd for $C_8H_8N_2$: C, 72.69; H, 6.11. Found: C, 72.76; H, 6.36.

C. 2-Cyano-3-cyclopropyl-2-butenamide (3). Condensation with Cyanoacetamide.—Following the heating period of 8 hr at 115°, the mixture was chilled, diluted with an equal volume of ligroin, and filtered to give slightly yellow crystals (73%), mp 125–155°, as a mixture of geometric isomers. Two recrystallizations from benzene, followed by one from 95% ethanol, afforded the higher melting isomer as colorless long needles: mp 167–168°; ir $\lambda_{\max}^{\mathrm{KBr}}$ 2.97 (s, NH_2), 3.15 (s, NH_2), 4.52 (m, C≡N), 6.08 (s, amide C=O), 6.34 (s, conjd C=C) μ; near-ir $\lambda_{\max}^{\mathrm{acetone}}$ 1.625 (m, cyclopropyl), and 2.2+ μ (absorption obscured by solvent).

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(9) W. H. Washburn and M. J. Mahoney, *J. Amer. Chem. Soc.*, **80**, 504 (1958).

(10) P. G. Gassman, *Chem. Ind.* (London), 740 (1962).

(11) D. W. Woodward, U. S. Patent 2,970,986 (1961); *Chem. Abstr.*, **55**, 12921 (1961).

(12) G. W. Cannon, R. C. Ellis, and J. R. Leal, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 597.

Anal. Calcd for $C_8H_{10}N_2O$: C, 63.97; H, 6.72; N, 18.66. Found: C, 64.12; H, 6.71; N, 18.80.

Reaction of 1 with Benzenethiol.—To a solution of 0.05 g (0.0022 g-atom) of sodium in 20 ml of absolute ethanol was added 3.3 g (0.03 mol) of benzenethiol and then 4.5 g (0.025 mol) of **1**, and the mixture was heated at reflux for 7 hr under argon. The ethanol was distilled under reduced pressure, and an ether solution of the residue was washed three times with water and once with saturated sodium chloride solution and dried ($CaCl_2$). Concentration under reduced pressure left 4.5 g of crude product which was distilled to give 3.5 g (48%) of colorless liquid (ethyl 2-cyano-3-methyl-6-phenylthio-2-hexenoate): bp 167–168° (0.2 mm); $n^{25}D$ 1.5558; near-ir $\lambda_{max}^{CCl_4}$ 1.72 (s), 1.79 (m), 2.18 (s), 2.29 (s), 2.33 (s), 2.38 (m), 2.44 (m), 2.50 (s) μ; ir $\lambda_{max}^{CCl_4}$ 4.5 (m, $C\equiv N$), 5.76 (s, ester $C=O$), 6.21 (s, $C=C$), 13.6 and 14.5 (s, C_6H_5) μ; nmr ($CDCl_3$) δ 7.25 (m, 5, C_6H_5), 4.22 (q, 2, OCH_2CH_3), 2.78 (m, 4, $SCH_2CH_2CH_2C=C$), 2.17 and 2.27 (each a singlet, *cis*- and *trans*-CH_3—C=C—), 1.86 (m, 2, $SCH_2CH_2CH_2C=C$), and 1.28 ppm (t, 3, OCH_2CH_3).

Anal. Calcd for $C_{16}N_{19}NSO_2$: C, 66.39; H, 6.63; N, 4.84. round: C, 66.28; H, 6.71; N, 4.88.

Reaction of 1 with 1-Butanethiol.—The reaction was carried out as described for thiophenol, using 2.75 g of 1-butanethiol. Final distillation gave 2.2 g of colorless liquid ethyl 2-cyano-3-methyl-6-butylthio-2-hexenoate: bp 142–143° (0.2 mm); $n^{25}D$ 1.4992.

Anal. Calcd for $C_{14}H_{23}NO_2S$: C, 63.36; H, 8.73. Found: C, 63.19; H, 8.50.

Both infrared and near-infrared spectra showed absorptions similar to the thiophenol product except for the absence of peaks due to the aromatic ring.

Reaction of 2 with Secondary Amines. Formation of Dimer.—A secondary amine (0.022 mol) was added at a fast rate dropwise to a solution of 2 g (0.015 mol) of **2** in 10–15 ml of absolute ethanol. Dimethylamine, diethylamine, or piperidine were used. A reaction occurred immediately, and after 1 hr, concentration under reduced pressure left a thick red oil which crystallized to a large extent after standing in the refrigerator for several days. Recrystallization (50% ethanol) gave yields of 0.5–1.3 g of light yellow crystals, mp 115–116°. A final recrystallization for an analytical sample was best accomplished from heptane: mol wt, calcd 264, found (benzene) 278; ir $\lambda_{max}^{CHCl_3}$ 2.88 (w, NH_2), 2.96 (m, NH_2), 4.55 (m, conjd $C\equiv N$), 6.1–6.16 (s), 6.34 (m, conjd $C=C$), 9.75 (m, broad, cyclopropyl), and 10.82 μ (w, broad, —C=C—H); nmr ($CHCl_3$) δ 5.71 (s, broad, 2, $-NH_2$), 4.62 and 4.65 [two singlets due to geometric isomers, 1, $-(NH_2)CH=C$], 1.23 (s, 3, $CH_3-C=C$), and 0.2–1.66 ppm (m, 10, two cyclopropyl).

Anal. Calcd for $C_{16}H_{16}N_4$: C, 72.69; H, 6.11; N, 21.20. Found: C, 72.91; H, 6.02; N, 21.37.

Transesterification of 1 with 1-Butanol in the Presence of Amines.—Diethylamine, piperidine, and morpholine all catalyzed this reaction to give the same single product in yields ranging from 32% for morpholine to 59% for the other two. The amine (0.048 mol) was dissolved in 20 ml of 1-butanol and added dropwise to a refluxing solution of 7.1 g (0.04 mol) of **1** in 30 ml of 1-butanol. The mixture was heated at reflux for an additional 2 hr and concentrated under reduced pressure, and the residue was distilled to give a colorless oil, *n*-butyl 2-cyano-3-cyclopropyl-2-butenoate: bp 109–110° (0.1 mm); $n^{25}D$ 1.5022.

Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.52; H, 8.28; N, 6.76. Found: C, 69.34; H, 8.41; N, 6.90.

The same transesterification could be effected by use of Triton B (ratio, 17 mol of compound 1/1 mole Triton B) in 22% yield.

Registry No.—**1** (solid), 17407-28-2; **1** (liquid), 17407-29-3; **2**, 17407-30-6; dimer of **2**, 17407-31-7; **3**, 17407-32-8; $C_{16}H_{19}NSO_2$ (*cis*), 17407-33-9; $C_{16}H_{19}NSO_2$ (*trans*), 17407-34-0; $C_{14}H_{23}NO_2S$, 17407-35-1; $C_{12}H_{17}NO_2$, 17407-36-2.

Acknowledgment.—This research was supported in part by a grant from the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is made to the donors of this fund. We are also grateful to Dr. Graeme Baker of Montana State University, Bozeman, Mont., fors ome of the nmr spectra.

Isomerization of Terpenes. The Isomerization of (−)-Perillaldehyde to *p*-Mentha-1,3-dien-7-al with Aqueous Sulfuric Acid

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Isomerization of some terpenoid compounds with aqueous acid or alkali has been observed by several workers. (−)-Perillaldehyde (**1**), however, has not yet been included in these investigations.

In the present paper, a monoterpene $\alpha\beta,\gamma\delta$-dienal, *p*-mentha-1,3-dien-7-al (**2**), was obtained from **1** on treatment with aqueous sulfuric acid. The same dienal structure as **2** has been assigned by Goryaev[1] to an oxidation product of sabinene with selenic acid and also by Matsuura[2] to one of the oxidation products of α-terpinene with *t*-butyl chromate, independently.

The apparent discrepancies in physical properties,[1,2] however, were found between the present authors' data and those by Matsuura and Goryaev. Based on the evidence to be presented below, it may be concluded that acid-catalyzed isomerization product of (−)-perillaldehyde is a monoterpene aldehyde, *p*-mentha-1,3-dien-7-al, different from the products described by Matsuura and Goryaev.

The isomerization of **1** was conducted in 10% aqueous sulfuric acid at 120–130° for 3 hr and afforded **2** in a 90% yield.

The absorption bands at 1666, 2700, and 2800 cm^{-1} in the ir spectrum of **2** are attributable to $\alpha\beta,\gamma\delta$-unsaturated aldehyde.[3-5]

In general, as the number of double bonds in conjugation increases, the $C=C$ vibration tends to shift progressively toward lower frequencies and enhance the intensity,[6] so that the strong absorption at 1570 cm^{-1} is reasonably attributed to $\alpha\beta,\gamma\delta$ double bond conjugated with carbonyl group. Matsuura, however, has reported no absorption band in this region.

In addition to the ir data, the spectral assignment of these chromophores is demonstrated by the maximum absorption at 315 mμ (ϵ 15,600) which is comparable with the accepted absorption maximum at 320 mμ for the conjugated dienone system according to the Fieser rule. The absorption maximum and intensity at 305 mμ (ϵ 4500) of the compound reported by Matsuura are not only inconsistent with the authors', but also lower than the values to be expected from the structure **2**.

Further evidence to support the structure of **2** was

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[1] M. I. Goryaev and G. A. Tolstikov [*Izv. Akad. Nauk SSSR, Ser. Khim.*, 72 (1962)] reported that the physical constants of the product were 2,4-DNPH mp 181–182° and semicarbazone mp 201–202°.

[2] T. Matsuura and T. Suga [*J. Org. Chem.*, **30**, 518 (1965)] reported that the physical constants of the product were ν_{max} 2750, 1670, 1375, 1357 cm^{-1}; λ_{max}^{MeOH} 305 mμ (ϵ 4500); 2,4-DNPH mp 230–231°, λ_{max}^{MeOH} 405 mμ (ϵ 28,000).

[3] A. Pozefsky and N. D. Coggeshall, *Anal. Chem.*, **23**, 1611 (1951).

[4] A. Ashdown and T. A. Kletz, *J. Chem. Soc.*, 1454 (1948).

[5] R. B. Turner and D. M. Voitle, *J. Amer. Chem. Soc.*, **73**, 1403 (1951).

[6] R. N. Jones, P. Humphries, E. Packard, and K. Dobriner, *ibid.*, **72**, 86 (1950).