Phenyl 2-Picolyl Ketone.—This ketone was prepared from 2-picolyllithium and benzoic anhydride by the method of Kloppenburg and Wibaut.[14] Thirty-five g. of 2-picoline gave 10.6 g. of ketone; yield 14%. The product was a bright yellow solid melting at 60–61.5° which did not darken on standing for over a year. Kloppenburg and Wibaut reported a melting point of 54° and Scheuing and Winterhalder[15] gave a melting point of 59°; picrate,[14] m.p. 179–180°; oxime,[15] m.p. 119°; hydrochloride, m.p. 174–176°.

Anal. Hydrochloride, Calcd. for $C_{13}H_{12}ONCl$: Cl, 15.17. Found: Cl, 14.95.

Hydantoins.—The hydantoins were prepared by the reaction of the ketones with KCN and $(NH_4)_2CO_3$. The method of Henze and Speer[5] was modified by extending the time to 48 hours. The reaction mixture was evaporated almost to dryness, made acid, and left overnight to allow HCN to escape. The mixture was made alkaline and extracted with ether, then made exactly neutral and evaporated to dryness. The hydantoin was extracted with alcohol from the large quantity of inorganic salt and recovered by evaporating the alcohol to dryness. The final purification was accomplished by recrystallization from diisobutyl ketone or a similar solvent. The results are summarized in Table I.

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[14] C. C. Kloppenburg and V. P. Wibaut, *Rec. trav. chim.*, **65**, 393 (1946).

[15] G. Scheuing and L. Winterhalder, *Ann.*, **473**, 126 (1929).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF CHAS. PFIZER AND CO., INC.]

Mycomycin. IV. Stereoisomeric 3,5-Diene Fatty Acid Esters[1]

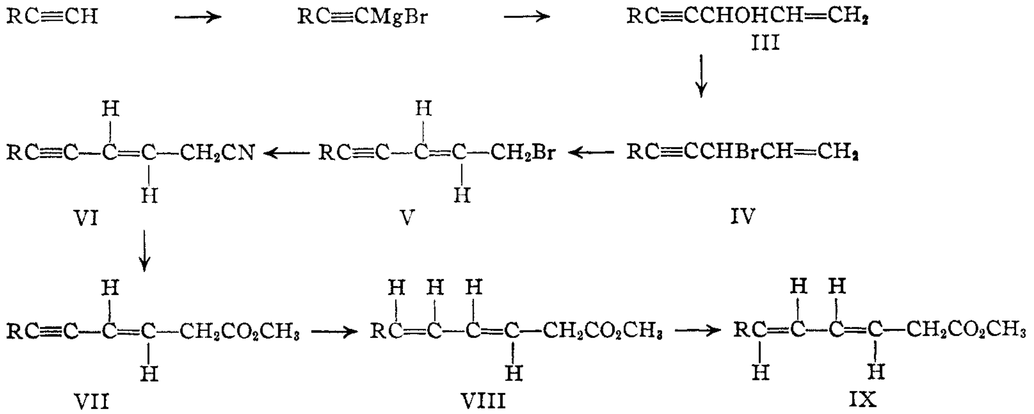
BY WALTER D. CELMER AND I. A. SOLOMONS

RECEIVED FEBRUARY 12, 1953

The synthesis of two stereoisomers of methyl 3,5-*n*-tridecadienoate, 3(*trans*),5(*cis*) and 3(*trans*),5(*trans*), through acetylenic intermediates is described. The synthesis is extended to the preparation of methyl 3(*trans*),5(*cis*) and 3(*trans*),5(*trans*)-*n*-nonadienoate. The 3,5-diene esters exhibit characteristic infrared absorption correlated with their stereochemical configuration. Two new examples of facile acetylene–allene isomerizations, noted in the course of this work, are discussed.

The deduced structures of both the antibiotic mycomycin, (−)3,5,7,8-*n*-tridecatetraene-10,12-diynoic acid, $HC{\equiv}C{-}C{\equiv}C{-}CH{=}C{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH_2{-}CO_2H$ (I) and its alkali-induced rearrangement product, isomycomycin, 3,5-*n*-tridecadiene-7,9,11-triynoic acid, $CH_3{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}CH{=}CH{-}CH{=}CH{-}CH_2{-}CO_2H$ (II), contain 3,5-diene groupings. With the question of their olefinic configurations remaining, stereoisomeric 3,5-diene fatty acids or their derivatives were sought as model compounds in the hope of facilitating geometric assignments. It is the purpose of this paper to describe, in detail, the synthesis and properties of 3(*trans*),5(*cis*) and 3(*trans*),5(*trans*) stereoisomers of methyl 3,5-*n*-tridecadienoate and methyl 3,5-*n*-nonadienoate. The correlations of the properties of the model diene esters with those of I and II have been discussed in a previous communication.[2] As a result of these studies, I and II were further characterized as possessing *trans,cis* and *trans,trans* stereo configurations, respectively.

The following diagram summarizes the steps used in the synthesis of the model compounds.[3]



a, R = *n*-C_3H_7 b, R = *n*-C_7H_{15}

The observed light absorption properties of the compounds involved in this synthesis were in agreement with their assigned structures and the linearity of VIIa as well as VIIb was established by reduction to the known saturated esters.

Compounds similar to the key intermediate halide V had been previously prepared by various

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[1] Presented in part before the Division of Medicinal Chemistry at the 122nd Meeting of the American Chemical Society, Atlantic City, September 17, 1952, and before the Chemical Society (London) Symposium on Acetylene Chemistry at Burlington House, February 5, 1953.

[2] W. D. Celmer and I. A. Solomons, THIS JOURNAL, **75**, 1372 (1953).

[3] The methyl esters of the desired acids were suitable models because of the availability of the methyl esters of I and II for comparison purposes (especially infrared spectra). The above scheme leads to the synthetic esters in a direct manner not involving the corresponding free acids. The latter were considered less desirable in this present study because of possible uncertainties regarding their homogeneity and were not investigated, *cf.* R. Paul and S. Tchelitcheff, *Compt. rend.*, **224**, 113 (1947); *Bull. soc. chim.* (*France*), 108 (1948).

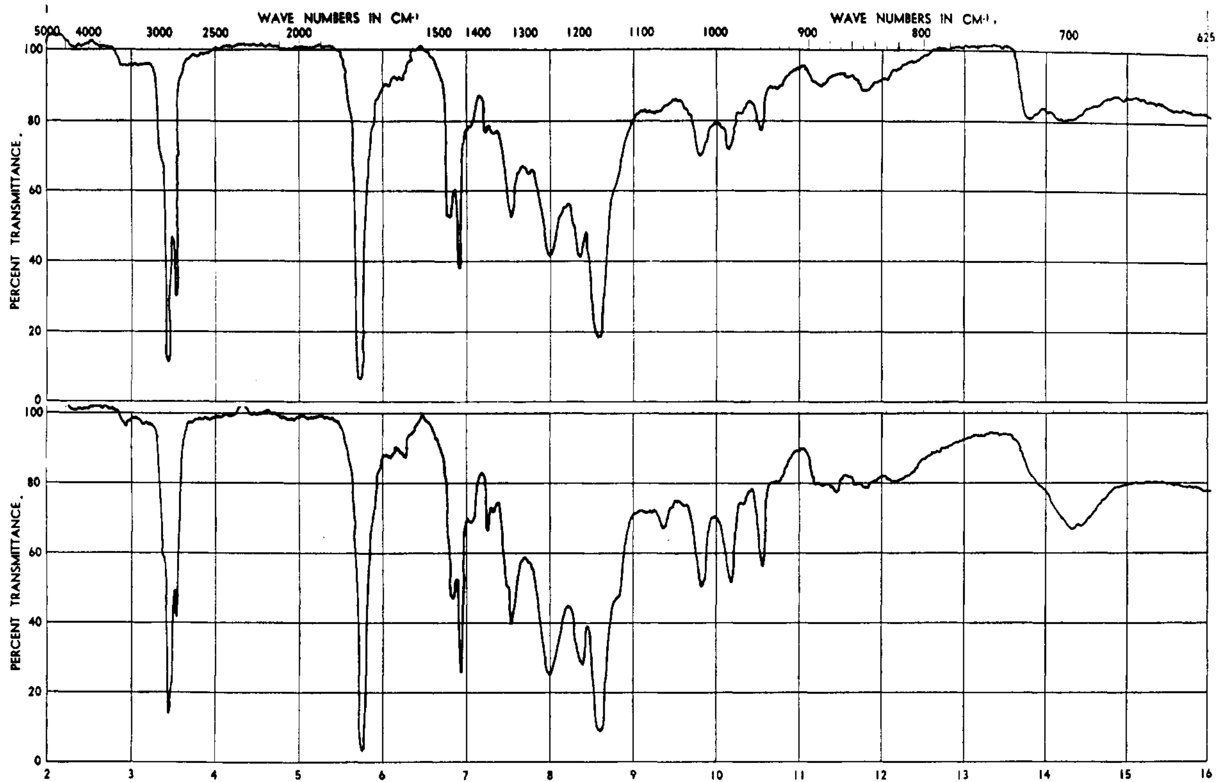

Fig. 1.—Infrared absorption spectra in carbon tetrachloride solution: upper, methyl 3(*trans*),5(*cis*)-*n*-tridecadienoate; lower, methyl 3(*trans*),5(*cis*)-*n*-nonadienoate.

routes.[4] In the present work, the secondary alcohols, IIIa and IIIb, initially obtained by the condensation of acrolein with the appropriate 1-alkynylmagnesium bromide, were brominated with phosphorus tribromide in the presence of pyridine.[5] The higher homolog, IIIb, yielded the primary bromide Vb exclusively, whereas, under the same conditions IIIa gave a mixture of the secondary and primary bromides, IVa and Va, in nearly equal amounts, separable by fractional distillation. The anionotropic rearrangements involved in the formation of Va and Vb were expected to yield the *trans* isomers, exclusively.[5,6] These primary halides were characterized by a strong infrared band near 950 cm.$^{-1}$ attributed to the *trans* olefinic configuration.[7]

The nitriles, VIa and VIb, obtained from the reaction of the corresponding halides with cuprous cyanide[8] were converted to the methyl esters, VIIa and VIIb, by the action of moist methanolic hydrogen chloride. The ene-ynoic esters were partially hydrogenated with the selective Lindlar catalyst[9] until one mole of hydrogen was consumed. The reduction products, VIIIa and VIIIb, were assigned the 3(*trans*),5(*cis*) configuration on the basis of (1) the known selectivity of the catalyst in forming *cis*-ethylenes by the semihydrogenation of acetylenes[10] and (2) their non-reactivity toward maleic anhydride.[11] Both VIIIa and VIIIb exhibited three characteristic infrared bands at *950*, *985* and *1020* cm.$^{-1}$ in the hydrogen bending region, associated with the stereochemical configuration about the 3(*trans*),5(*cis*) diene groupings[2,12] (Fig. 1).

The 3(*trans*),5(*cis*) dienes were converted catalytically to the corresponding *trans,trans* isomers, IXa and IXb, with iodine.[13] The course of the isomerization was conveniently followed by infrared spectral measurements and was assumed to be complete after full development of a strong band at 990 cm.$^{-1}$, attributed to the *trans,trans*-diene grouping[2,12] (Fig. 2). The ultraviolet light absorption properties also changed significantly during the isomerization from $\lambda_{\max}$ 233 mμ to $\lambda_{\max}$

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[4] I. M. Heilbron, E. R. H. Jones, R. N. Lacey, J. T. McCombie and R. Raphael, *J. Chem. Soc.*, 77 (1945); H. B. Henbest, E. R. H. Jones and I. M. S. Walls, *ibid.*, 3646 (1950).

[5] M. Bouis, *Ann. chim.*, **9**, 402 (1928).

[6] S. Winstein and W. G. Young, THIS JOURNAL, **58**, 104 (1936); E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2085 (1951); L. Crombie, *Quart. Revs.* (*London*), **6**, 101 (1952).

[7] Simple *trans* olefins exhibit a strong characteristic infrared band in the hydrogen bending region near 970 cm.$^{-1}$ [*cf.* R. S. Rasmussen, R. R. Brattain and P. S. Zucco, *J. Chem. Phys.*, **15**, 135 (1947); O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *Anal. Chem.*, **22**, 1261, 1498 (1950)]. When conjugated with an acetylenic bond, the *trans* olefin apparently exhibits strong absorption at a somewhat lower frequency, *i.e.*, 950 cm.$^{-1}$.

[8] The infrared spectra of the ene-ynoic nitriles and esters also exhibited a strong 950 cm.$^{-1}$ band; *cf.* footnote 7.

[9] H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

[10] See footnote 13 in the recent paper by F. Sondheimer, THIS JOURNAL, **74**, 4040 (1952).

[11] *Cf.* D. Craig, *ibid.*, **72**, 1678 (1950); K. Alder and M. Schumacher, *Ann.*, **571**, 87 (1950); J. D. Von Mikusch, *Angew. Chem.*, **62**, 475 (1950).

[12] *Cf.* J. E. Jackson, R. F. Paschke, W. Tolberg, H. M. Boyd and D. H. Wheeler, *J. Am. Oil Chem. Soc.*, **29**, 229 (1952); N. Sheppard and D. M. Simpson, *Quart. Revs.* (*London*), **6**, 1 (1952).

[13] *Cf.* (a) A. Sandoval and L. Zechmeister, THIS JOURNAL, **69**, 553 (1947); (b) P. L. Nichols, Jr., S. F. Herb and R. W. Riemenschneider, *ibid.*, **73**, 247 (1951).

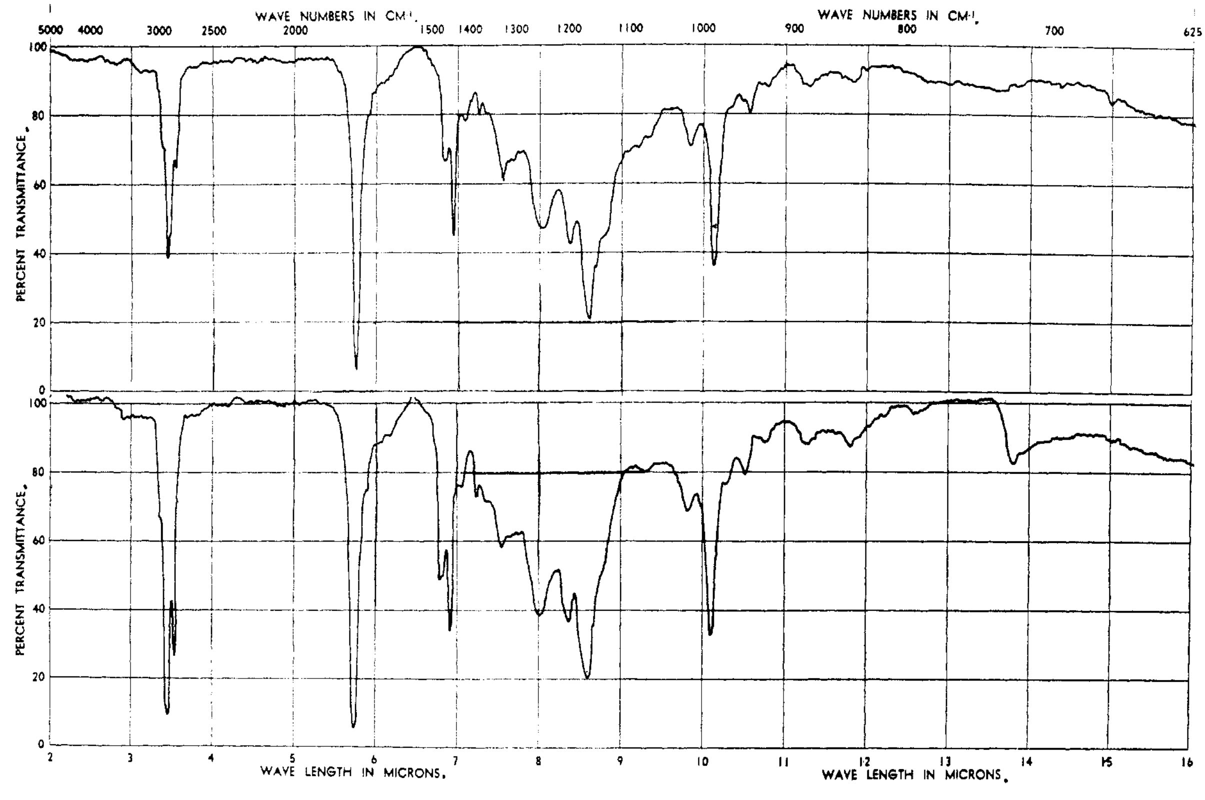
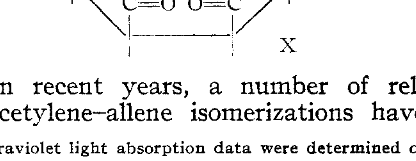


Fig. 2.—Infrared absorption spectra in carbon tetrachloride solution: upper, methyl 3(*trans*),5(*trans*)-*n*-tridecadienoate; lower, methyl 3(*trans*),5(*trans*)-*n*-nonadienoate.

228–229 mμ.[14] This behavior is also observed with isolinoleic acids.[15] Apparently, the lower ground state of the *trans,trans* compounds is influential in shifting the ultraviolet light absorption maxima to shorter wave lengths.[16]

As expected,[11] both *trans,trans* products, IXa and IXb, condensed readily with maleic anhydride and crystalline products were obtained. Hydrogenation of the maleic anhydride adduct of IXb gave the reduction product, 6-(*cis*)-*n*-heptyl-1 (*cis*),2(*cis*)-cyclohexanedicarboxylic anhydride 3-acetic acid methyl ester (X), which possessed an infrared spectrum and a refractive index identical with those exhibited by the tetradecahydroderivative of the maleic anhydride adduct of isomycomycin methyl ester.[17] The deduced structure of isomycomycin[18] is in accord with these findings.



X

Within recent years, a number of relatively facile acetylene–allene isomerizations have been observed.[19] In the course of the present synthetic work, two new examples of such isomerizations have been detected: (1) mild saponification of $R{-}C{\equiv}C{-}CH{=}CH{-}CH_2CO_2CH_3$ (VIIa and VIIb) yielded a mixture of products believed to be the normal acid and an allenic compound, most likely $R{-}CH{=}C{=}CH{-}CH{=}CH{-}CO_2H$ (XI), evidenced by the infrared spectra of the crude acids, which clearly disclosed both a disubstituted acetylenic band at 2200 cm.$^{-1}$ [20] and an allenic band at 1930 cm.$^{-1}$ [21,22] (Fig. 3). Fractional low temperature crystallizations from hexane afforded the acetylenic component and enrichment of the allene in the mother liquors. Exhaustive distillation of the purified allene gave distillates containing only

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(14) Ultraviolet light absorption data were determined on alcohol solutions using both the Beckman and Cary instruments.

(15) Conjugated (*cis*), (*trans*)-isolinoleic acids possessed ultraviolet absorption maxima at 232–233 mμ, while the *trans,trans* isomers disclosed maxima at measurably lower wave lengths, *ca.* 227–229 mμ (*cf.* footnote 13b).

(16) L. N. Ferguson, *Chem. Revs.*, **43**, 385 (1948).

(17) W. D. Celmer and I. A. Solomons, THIS JOURNAL, **74**, 3838 (1952).

(18) W. D. Celmer and I. A. Solomons, *ibid.*, **74**, 1870 (1952).

(19) Interest in these isomerizations was aroused by the remarkable ease with which the antibiotic mycomycin was rearranged to isomycomycin by cold, dilute caustic, *cf.* footnote 17. Reports from the University of Manchester, England, have disclosed a variety of facile base-induced acetylene–allene isomerizations encountered with synthetic compounds, *cf.* E. R. H. Jones, paper presented before the Division of Organic Chemistry at the 120th Meeting of the American Chemical Society, New York, September 6, 1951; M. C. Whiting, paper presented before the Chemical Society (London) Symposium on Acetylene Chemistry at Burlington House, February 5, 1953.

(20) J. H. Wotiz and F. A. Miller, THIS JOURNAL, **71**, 3441 (1949).

(21) J. H. Wotiz and W. D. Celmer, *ibid.*, **74**, 1860 (1952); R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 131 (1947).

(22) Available physical evidence supports the suggested formulation XI for the allenic component. Notably (Fig. 3), a strong band near 1625 cm.$^{-1}$ is in accord with an α,β-olefinic acid [*cf.* J. Cason, N. K. Freeman and G. Sumrell, *J. Biol. Chem.*, **192**, 415 (1951)]. Furthermore, the ultraviolet absorption spectra of the crude saponification mixtures from VIIa and VIIb exhibited maxima near 265 and 235 mμ. The absorption at the longer wave length, 265 μ, is expected of the chromophore in XI, which includes conjugated allenic, olefinic and carbonyl bonds (ref. 2), whereas, the 235 mμ absorption is typical of the conjugated ene-yne chromophore.

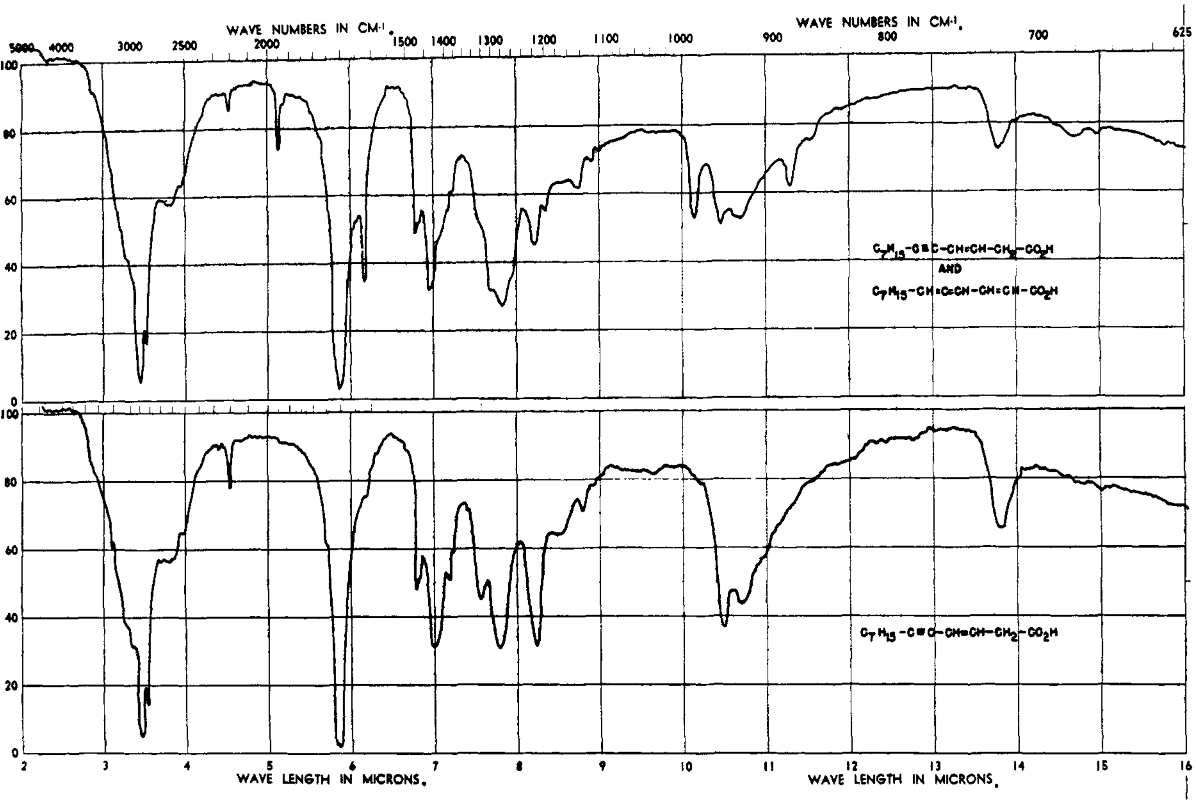

Fig. 3.—Infrared absorption spectra in carbon tetrachloride solution: upper, mixture of acetylenic and allenic acids from the saponification of methyl 3(*trans*)-*n*-tridecaen-5-ynoate; lower, acetylenic component isolated from the above saponification products by fractional crystallization.

the acetylenic product. Acid hydrolysis of VII yielded only the normal acetylenic product (Fig. 3). (2) The Reformatsky condensation of zinc propargyl bromide and butyraldehyde reported to yield 1-heptyn-4-ol,[23] gave in addition an allenic compound, believed to be 1,2-heptadien-4-ol (XII). The infrared spectrum of the crude distilled product exhibited both monosubstituted acetylenic (3350 and 2140 cm.$^{-1}$)[20] and allenic (1970 cm.$^{-1}$)[21,24] absorption (Fig. 4). The purified allenic alcohol (Fig. 4) was obtained from the mixture after removing the acetylenic component as its insoluble silver salt.

Experimental[25]

1-*n*-Dodecaen-4-yn-3-ol (IIIb).—The alkynyl Grignard compound was prepared in the usual manner using 1-nonyne (93 g.) in dry ether (50 ml.) and ethereal ethylmagnesium bromide (330 ml. of a 2.8 *N* solution). Acrolein (50.4 g.) in dry ether (60 ml.) was added dropwise during 30 minutes to the cooled (ice–water) and stirred reaction mixture, which was then stirred for three hours more. An excess of saturated aqueous ammonium chloride solution was added, the ether layer separated, and the aqueous layer extracted with additional ether. The combined ethereal extracts were washed with water, dried (Na_2SO_4) and evaporated under reduced pressure. Distillation of the residue afforded IIIb (75 g., 56% yield), as a colorless liquid, b.p. 69–72° (0.45 mm.), $n^{25}D$ 1.4612.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.99; H, 11.23.

1-*n*-Octaen-4-yn-3-ol (IIIa).—The above procedure was applied to 1-pentyne and acrolein. The product (IIIa) was obtained in 47% yield as a colorless liquid, b.p. 46–48° (0.18 mm.), $n^{25}D$ 1.4642.

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.24; H, 9.54.

Neither IIIa nor IIIb exhibited ultraviolet light absorption above 219 mμ, which is in accord with their non-conjugated structures.

1-Bromo-2(*trans*)-*n*-dodecaen-4-yne (Vb).—The general procedure of Bouis[5] was used. To a cooled (ice–water) stirred solution of IIIb (54 g.) in dry ether (100 ml.) containing dry pyridine (2.4 g.) was added dropwise during 15 minutes a solution of phosphorus tribromide (42.7 g.) in dry ether (30 ml.). The reaction mixture was then heated under slow reflux for 20 minutes. After cooling, the upper layer was poured onto ice. The organic layer was recovered, washed successively with water, sodium carbonate and water, dried (Na_2SO_4) and evaporated under reduced pressure. Distillation of the residue gave Vb (58.8 g., 81% yield) as a colorless liquid, b.p. 81–85° (0.3 mm.), $n^{25}D$ 1.5098, λ_{max} 240 mμ, ϵ 14,000.

Anal. Calcd. for $C_{12}H_{19}Br$: C, 59.26; H, 7.88; Br, 32.92. Found: C, 59.28; H, 7.82; Br, 32.87.

The infrared spectrum of Vb (carbon tetrachloride solution) exhibited a strong band at 950 cm.$^{-1}$[7] with no apparent vinyl absorption near 920 and 980 cm.$^{-1}$, which suggested the absence of significant amounts of the non-isomerized compound, 3-bromo-1-dodecaen-4-yne.[26]

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[23] H. B. Henbest, E. R. H. Jones and I. M. S. Walls, *J. Chem. Soc.*, 2696 (1949).

[24] The formation of allenic products in this Reformatsky reaction was not unexpected. The zinc–copper treatment of propargylic halides has yielded allenes among the dehalogenation products [*cf.* G. F. Hennion and J. J. Sheehan, THIS JOURNAL, **71**, 1964 (1949); J. H. Wotiz, *ibid.*, **73**, 693 (1951)].

[25] Ultraviolet light absorption data were obtained on alcohol solutions. Melting points were determined on a Kofler apparatus and are corrected. Boiling points were observed during short path distillations with different vacuum systems and flasks, and are subject to the obvious limitations of this method. Except where noted, the distillate forerun, middle cut and tailings exhibited indistinguishable infrared spectra and only slight variation in refractive indexes. A sample of the middle cut was taken for analyses.

[26] H. W. Thompson, *J. Chem. Soc.*, 328 (1948).

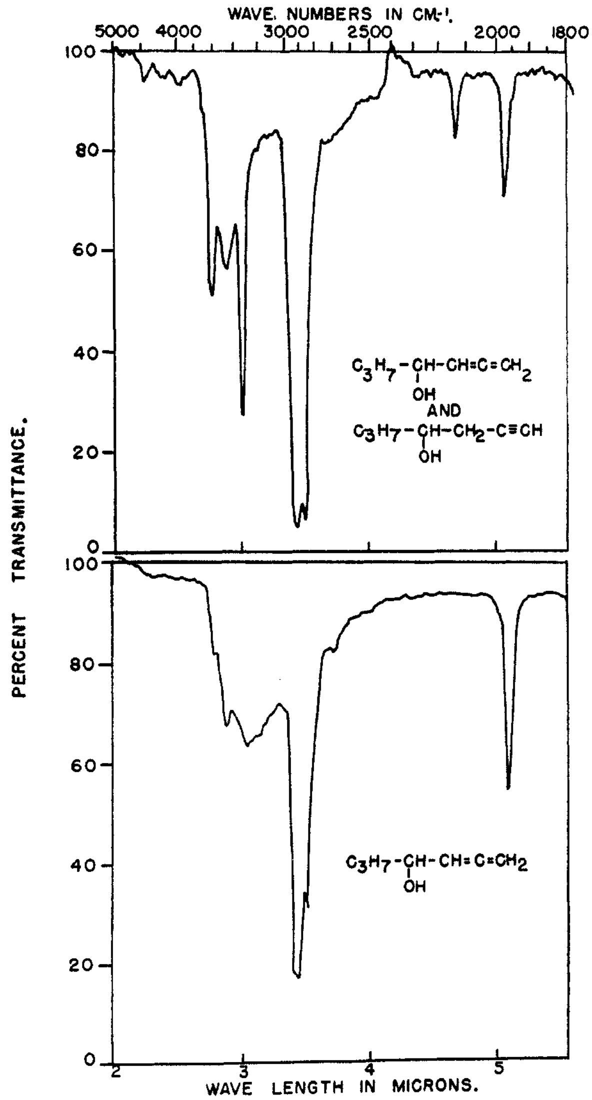

Fig. 4.—Infrared absorption spectra in carbon tetrachloride solution: upper, mixture of allenic and acetylenic alcohols from the Reformatsky reaction of butyraldehyde and zinc propargyl bromide; lower, allenic component from the above reaction products.

1-Bromo-2(*trans*)-*n*-octaen-4-yne (Va).—The bromination procedure of Bouis[5] was also applied to IIIa, as described above. The product (75% yield) distilled over a range of 28–36° (0.08 mm.). The highest boiling material exhibited intense ultraviolet absorption above 220 mμ, whereas the lowest boiling fraction was relatively light-transparent in this region. Quantitative determinations based on ultraviolet light absorption of the crude product relative to the light absorption of the highest boiling material ("pure" Va) revealed that Va represented about 60% of the total product. The best preparation of Va possessed the following properties, b.p. 35–36° (0.08 mm.), $n^{25}D$ 1.5300, λ_{max} 245 mμ, ε 15,000.

Anal. Calcd. for $C_8H_{11}Br$: C, 51.36; H, 5.93. Found: C, 50.18; H, 5.88.

The ultraviolet-inactive material, b.p. 28–33° (0.08 mm.), $n^{25}D$ 1.5080, was assumed to be mostly 3-bromo-1-octaen-4-yne (IVa). The infrared absorption spectrum (carbon tetrachloride solution) of IVa exhibited two characteristic strong bands associated with its vinyl grouping[26] near 920 and 980 cm.⁻¹, whereas Va exhibited a strong band near 950 cm.⁻¹ (similar to Vb) with no vinyl absorption. On standing or after treatment with mineral acid, IVa was converted to Va, evidenced by the changes in ultraviolet light absorption properties and infrared spectra.

The bromo compounds described above were lachrymatory, darkened on standing and immediately precipitated silver bromide when treated with alcoholic silver nitrate. The primary halides were converted to the nitriles without delay.

1-Cyano-2(*trans*)-*n*-dodecaen-4-yne (VIb).—A mixture of Vb (6 g.), cuprous cyanide (3 g.) and sodium iodide (0.05 g.) in *p*-xylene (5 ml.) was heated cautiously until the solvent refluxed slowly. After a few minutes, a vigorous exothermic reaction ensued and the reaction mixture darkened. Heating was continued until tests on withdrawn samples indicated that no organic halide remained (1 hour). After cooling, the reaction mixture was exhaustively extracted with ether (20 ml., 5 times). The filtered ether extracts were combined and evaporated *in vacuo*. The dark product was distilled under reduced pressure; b.p. 100–101° (0.45 mm.), $n^{25}D$ 1.4789, λ_{max} 227 mμ, ε 14,000; λ_{max} 236 mμ, ε 13,000, yield 1.4 g. (31%).

Anal. Calcd. for $C_{13}H_{19}N$: N, 7.44. Found: N, 6.99.

1-Cyano-2(*trans*)-*n*-octaen-4-yne (VIa).—In a manner similar to the above, Va was converted to VIa in 41% yield; b.p. 53–55° (0.7 mm.), $n^{25}D$ 1.4827, λ_{max} 227 mμ, ε 14,000; λ_{max} 235 mμ, ε 12,000.

Anal. Calcd. for $C_9H_{11}N$: C, 81.16; H, 8.33. Found: C, 82.13; H, 8.06.

The nitriles (disagreeable odors) were initially obtained as colorless liquids[18] but rapidly darkened, hence they were converted to the esters as soon as possible.

Methyl 3(*trans*)-*n*-Tridecaen-5-ynoate (VIIb).—A slow stream of hydrogen chloride (tank) was bubbled into a solution of VIb (3.1 g.) in methanol (10 ml.) containing water (1 ml.). The resulting heat of reaction caused the solvent to reflux and after the temperature had subsided (10 minutes), the reaction mixture was poured onto ice and the organic layer extracted with pure ether. The ether extract was washed successively with water, sodium carbonate and water, dried (Na_2SO_4) and evaporated. The residue was distilled to give VIIb, 2.8 g. (80% yield), as a colorless liquid, b.p. 100–102° (0.5 mm.), $n^{25}D$ 1.4730, λ_{max} 227 mμ, ε 13,000, λ_{max} 235.5 mμ, ε 12,000.

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.68; H, 9.91. Found: C, 75.84; H, 9.95.

Methyl 3(*trans*)-*n*-Nonaen-5-ynoate (VIIa).—In a similar way, as described above, and in comparable yield, VIa was converted to VIIa; b.p. 56–58° (0.2 mm.), $n^{25}D$ 1.4768, λ_{max} 227 mμ, ε 17,000, λ_{max} 235 mμ, ε 11,000.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.07; H, 8.49.

The methyl esters VIIa and VIIb were much more stable than the corresponding nitriles. Complete hydrogenation (Adams catalyst) required three moles of hydrogen. The reduction products exhibited infrared spectra indistinguishable from those of methyl pelargonate and methyl *n*-tridecanoate, respectively. Saponification of hydrogenated VIIb gave a crystalline acid, m.p. 39–40°, identified as *n*-tridecanoic acid.

Methyl 3(*trans*),5(*cis*)-*n*-Tridecadienoate (VIIIb).—A prereduced Lindlar catalyst preparation[9] consisting of palladium and lead on calcium carbonate (5 g.) and quinoline (0.1 g.) in ethyl acetate (15 ml.) was treated with VIIb (1.11 g.) in ethyl acetate (15 ml.) and stirred magnetically under one atmosphere of hydrogen at 34°. A volume of hydrogen corresponding to one equivalent had been taken up after 20 minutes and the hydrogenation was interrupted. The reaction mixture was filtered, the catalyst washed with ethyl acetate, and the solvent was evaporated. A solution of the residue in pure ether was washed successively with cold dilute sulfuric acid (to remove quinoline) and water, dried (Na_2SO_4) and evaporated. The product was purified by distillation to give 1.01 g. (90% yield) of a colorless liquid, b.p. 93–94° (0.17 mm.); $n^{25}D$ 1.4663, λ_{max} 233 mμ, ε 17,000.

Anal. Calcd. for $C_{14}H_{24}O_2$: C, 75.01; H, 10.71. Found: C, 75.06; H, 10.81.

Methyl 3(*trans*),5(*cis*)-*n*-Nonadienoate (VIIIa).—Partial hydrogenation of VIIa was conducted as described above. The product, VIIIa, was recovered in 86% yield as a colorless liquid, b.p. 50–52° (0.05 mm.), $n^{25}D$ 1.4690, λ_{max} 233 mμ, ε 19,000.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.68; H, 9.43.

The infrared spectra of VIIIa and VIIIb are recorded in Fig. 1. Complete catalytic hydrogenation (Adams catalyst) of VIIIa or VIIIb required two moles of hydrogen. Neither VIIIa nor VIIIb exhibited detectable reactivity toward maleic anhydride, either fused at 100° for 3 hours or in refluxing toluene solution for 18 hours.[27]

Methyl 3(*trans*),5(*trans*)-*n*-Tridecadienoate (IXb).—A solution of VIIIb (0.6 g.) in carbon tetrachloride (6 ml.) was treated with iodine (0.3 ml. of 0.1 *N* in carbon tetrachloride). The reaction mixture was allowed to stand in a glass stoppered Pyrex flask (50-ml. capacity) exposed to ordinary diffuse laboratory light at approximately 32°. The course of the isomerization was followed by periodic infrared spectral determinations and after 72 hours, a strong band at 990 cm.$^{-1}$ (attributed to a *trans,trans* configuration) had reached a constant maximum intensity and the isomerization was assumed to be complete. The solvent was evaporated by a stream of nitrogen and the residue distilled. The product, IXb, 0.48 g. (80% yield), was obtained as a colorless liquid, b.p. 97–100° (0.4 mm.), $n^{25}\mathrm{D}$ 1.4631, $\lambda_{\max}$ 229 mμ, ϵ 14,000.

Anal. Calcd. for $C_{14}H_{24}O_2$: C, 75.01; H, 10.71. Found: C, 75.13; H, 10.28.

A mixture of IXb (0.22 g.) and maleic anhydride (0.1 g.) was fused in a sealed tube and the solution heated for 2 hours at 85°. After cooling, the resulting crystalline solid was extracted with warm hexane which deposited white crystals upon cooling, 0.25 g., m.p. 92–95°. Recrystallization from hexane yielded colorless plates, m.p. 94–96°.

Anal. Calcd. for $C_{18}H_{26}O_5$: C, 67.06; H, 8.13. Found: C, 66.55; H, 8.23.

This maleic anhydride adduct dissociated at elevated temperatures under reduced pressure. A solution of the maleic anhydride adduct of IXb (10.5 mg.) in ethyl acetate (5 ml.) was stirred with Adams catalyst (50 mg.) in an atmosphere of hydrogen at 27° for 45 minutes. The filtered solution was evaporated and the product (X) was obtained as a viscous oil, $n^{25}\mathrm{D}$ 1.4780 ± 0.0005. Its infrared spectrum (carbon tetrachloride solution) was indistinguishable from that of the tetradecahydro derivative of the maleic anhydride adduct of isomycomycin methyl ester, reported[17] as an oil, $n^{25}\mathrm{D}$ 1.4780.

Methyl 3(*trans*),5(*trans*)-*n*-Nonadienoate (IXa).—Repetition of the above iodine isomerization conditions using VIIIa gave IXa in 84% yield, b.p. 49–50° (0.09 mm.), $n^{25}\mathrm{D}$ 1.4672, $\lambda_{\max}$ 228 mμ, ϵ 17,000.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.26; H, 9.74.

The maleic anhydride adduct of IXa was prepared as described above, m.p. 90–91°.

Anal. Calcd. for $C_{14}H_{18}O_5$: C, 63.16; H, 6.77. Found: C, 63.12; H, 7.00.

The infrared spectra of IXa and IXb are recorded in Fig. 2. The rate of the above isomerization could be increased by supplying additional illumination[13a] but lower yields were realized.

Acetylene–Allene Isomerizations. Saponification of VIIa.—A solution of VIIa (1.7 g.) in methanol (75 ml.) and water (25 ml.) containing 5.6 g. of potassium hydroxide was allowed to stand at room temperature for 1 hour after which time an ether extraction indicated the absence of non-saponified material. After cooling, water (200 ml.) and ether (200 ml.) were added and the reaction mixture was acidified to *p*H 2 with dilute hydrochloric acid. The ether phase was collected, washed with water, dried (Na_2SO_4) and evaporated, *in vacuo*. The residue (1.4 g.) was obtained as a light amber liquid. Its infrared spectrum (carbon tetrachloride solution) disclosed both disubstituted acetylenic (2200 cm.$^{-1}$)[20] and allenic (1930 cm.$^{-1}$)[21,22] absorption bands, indicating that a mixture of isomeric acids had been obtained. Attempts to separate the isomers by low temperature (−80°) crystallization from hexane gave the acetylenic component in the crystalline fractions and an enrichment of the allene in the mother liquors. Surprisingly, exhaustive distillation of the allene-rich fractions gave only the acetylenic component suggesting that it was the more stable isomer. Acid hydrolysis of VIIa (1.7 g.) in dioxane (25 ml.) water (10 ml.), and concentrated hydrochloric acid (0.5 ml.) refluxed for 0.5 hour, gave only the normal product, 3-*n*-nonaen-5-ynoic acid, as indicated by the infrared spectra of the crude and distilled product. Distillation gave a colorless liquid, 1.2 g., b.p. 86–88° (0.08 mm.), $n^{25}\mathrm{D}$ 1.4870.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.03; N, 7.84.

The above saponification procedure applied to VIIb also gave a mixture of acetylenic and allenic products (Fig. 3).

Acetylene–Allene Isomerizations. Reformatsky Reaction.—Attempts to prepare 1-heptyn-4-ol[23] by the Reformatsky reaction of butyraldehyde and zinc propargyl bromide invariably gave a mixture of acetylenic and allenic products. The procedure of Henbest, *et al.*,[23] was closely followed and a colorless liquid was obtained in comparable yield, as reported for 1-heptyn-4-ol, b.p. 63–65° at 16 mm. (lit.[23] 58–59° at 11 mm), $n^{25}\mathrm{D}$ 1.4441 (lit.[23] $n^{20}\mathrm{D}$ 1.4443). The infrared spectrum of this material exhibited both monosubstituted acetylenic absorption (3350 and 2140 cm.$^{-1}$)[20] and allenic absorption (1970 cm.$^{-1}$)[21]; disubstituted acetylenic absorption was absent (Fig. 4). Rectification of the product gave enrichment of the allenic product in the lower boiling cuts but the boiling point proximity of the isomers made this an inefficient method of separation. A more promising means of fractionating the mixture was realized by removing the acetylenic component as its insoluble silver salt, leaving the allenic alcohol in solution (Fig. 4). This method indicated that the ratio of acetylene: allene components was close to one.

The same procedure[23] applied to octanal also gave a mixture of acetylenic and allenic products, b.p. 119–120° (16 mm.), $n^{25}\mathrm{D}$ 1.4499, whereas benzaldehyde gave only the acetylenic product, as reported.[23]

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[27] O. Grummitt and F. J. Christoph, THIS JOURNAL, **73**, 3479 (1951).