phenylpropiolate.—The crude ester (1.35 g) was dissolved in acetic anhydride (25 ml) and heated under reflux for 11 hr, the solvent removed under reduced pressure, and the residue subjected to thin layer chromatography on silica gel PF (1.0 mm) using ethyl acetate–chloroform (1:9). Two principal zones (R_f 0.46 and 0.53) which overlapped were separated and eluted, and the chromatographic treatment was repeated.

Crystallization of the slower running component from acetone–petroleum ether (bp 60–110°) and then propanol yielded **3,4-dihydro-6,7-dimethoxy-3-hydroxymethyl-1-(3′,4′-methylenedioxyphenyl)naphthalene-2-carboxylic acid lactone** [(±)-**collinusin**] (I) as a white solid (121 mg): mp 195–198°; ν (KBr) 1742 (conj γ-lactone), 1626, 1603, 1565, 1502 and 928 cm^{-1}; λ (C_2H_5OH) 248 nm (log ϵ 4.18) and 344 (3.99); δ 3.66 s (C-7 methoxyl), 3.90 s (C-6 methoxyl), 5.98 s (methylenedioxy group), 6.57 s (H-8), 6.80 br (four Ar H), and 2.67–4.82 complex m (5 protons; benzylic, allylic, and lactone methylene protons).

Anal. Calcd for $C_{21}H_{18}O_6$: C, 68.84; H, 4.95. Found: C, 68.36; H, 5.17.

Crystallization of the faster running component from methylene chloride–petroleum ether (bp 38–54°) yielded **3,4-dihydro-7,8-dimethoxy-3-hydroxymethyl-1-(3′,4′-methylenedioxyphenyl)-naphthalene-2-carboxylic acid lactone** (VI) as a white solid (63 mg): mp 213–215°; ν 1748 (conj γ-lactone), 1631, 1542, 1484, and 937 cm^{-1}; λ (C_2H_5OH) 240 nm (log ϵ 4.13) and 295 (4.15); δ 3.22 s (C-8 methoxyl), 3.80 s (C-7 methoxyl), 5.96 s (methylenedioxy group), 6.80–6.95 (five Ar H), and 2.62–5.40 complex m (5 protons, benzylic, allylic, and lactone methylene protons).

Anal. Calcd for $C_{21}H_{18}O_6$: C, 68.84; H, 4.95. Found: C, 69.04; H, 5.00.

Elution of a still faster running zone (R_f 0.62) yielded an oil (48 mg) identified as **3,4-dimethoxycinnamyl acetate** (IV, R = $COCH_3$)[35] by comparison with an authentic sample prepared by treatment of 3,4-dimethoxycinnamyl alcohol with acetic anhydride in pyridine. It had ν 1730 (carbonyl) and 966 cm^{-1} (trans alkene); δ 2.08 s (acetate methyl group), 3.87 s and 3.88 s (methoxyl groups), 4.72 d (J = 6 Hz, allylic CH_2), 5.90–6.72 m (two vinyl protons), and 6.77–7.12 m (three Ar H).

Conversion of (±)-Collinusin to Justicidin B.—A mixture of collinusin (25.5 mg), *N*-bromosuccinimide (15 mg), and benzoyl peroxide (2 mg) in carbon tetrachloride (20 ml) was heated under reflux for 10 min during which time the solution turned yellow and then for a further 20 min after which time the color had been discharged. The cooled and filtered solution was evaporated under reduced pressure and the residue chromatographed on a silica gel PF plate (1.0 mm) with ethyl acetate–chloroform (1:9). Elution of the zone R_f 0.31 yielded a product (24 mg) which on crystallization from acetone–ether gave **6,7-dimethoxy-3-hydroxymethyl-1-(3′,4′-methylenedioxyphenyl)naphthalene-2-carboxylic acid lactone** (**justicidin** B) (II) as needles: mp 237–238° (lit.[31] mp 240°); ν (KBr) 1761 (lactone), 1623 and 933 cm^{-1}; λ ($CHCl_3$) 260 nm (log ϵ 4.77), 296 (4.02), 308 (4.02), and 350 (3.73); δ 3.80 s (C-7 methoxyl), 4.03 s (C-6 methoxyl), 5.37 d (J = 1 Hz, lactone methylene), 6.00 d and 6.07 d (J = 1.5 Hz, methylenedioxy group), and 6.75–7.70 (five Ar H).

Registry No.—I, 28982-10-7; II, 17951-19-8; III, 31337-55-0; IV (R = H), 18523-76-7; IV (R = $COCH_3$), 31337-58-3; V, 28908-38-5; VI, 31337-60-7.

(35) E. Adler and B. Gustafsson, *Acta. Chem. Scand.*, **17**, 27 (1963).

Base-Catalyzed Rearrangement of ω-Bromolongifolene

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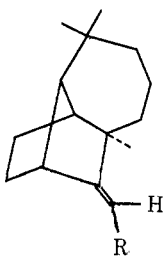
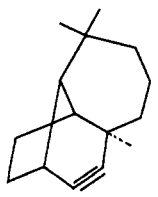
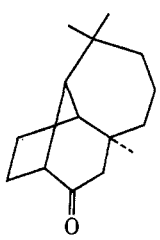
We wish to report here the generation and capture of a highly strained tricycloalkyne,[1] the 3,8,8-trimethyltricyclo[7.3.0.0^{4,10}]dodec-2-yne (**3**) (longifolyne), *via* a base-induced Fritsch–Buttenberg–Wiechell rearrangement[2] of ω-bromolongifolene (**2**). Bhattacharyya and coworkers[3] have recently reported that fusion of **2** with potassium hydroxide at 400° gave a mixture of ring-expanded ketones, longihomocamphenilone (**4**) and longiisohomocamphenilone (**5**), in 5–7% yield together with a dimeric dilongifolenyl ether (**6**). The nature of the ring enlargement products was suggestive of the possible intermediacy of cycloalkyne **3** in the alkali fusion reaction. The intervention of **3** in the rearrangement of ω-bromolongifolene with potassium *tert*-butoxide is described here.



1, R = H
2, R = Br



3



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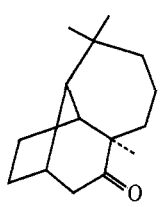

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Longifolene (**1**) was converted into ω-bromolongifolene (**2**) in one step *via* vinylic bromination with *N*-bromosuccinimide in refluxing benzene. The diagonistic feature of the nmr spectrum was the appearance of the olefinic proton singlet at τ 4.37 and an allylic bridgehead proton signal at τ 6.87 [*cf.* longifolene (**1**) at τ 7.42]. The strong deshielding[4] of the allylic bridgehead proton leads to assignment of bromine as anti with respect to the large ring. This is in conformity with the X-ray crystal structure[5] of **2**. On refluxing with potassium *tert*-butoxide in toluene the ω-bromomethylene derivative **2** readily rearranged to cycloalkyne **3** and was trapped with 1,3-diphenylisobenzofuran to furnish an adduct, mp 254–256°, in 85% yield. The adduct is devoid of any olefinic proton absorption in the nmr spectrum but exhibits signals at τ 9.11, 9.30, and 9.51 (3 H, s, Me), 7.25 (1 H, broad, allylic bridgehead), and 1.8–1.3 (14 H, m, aromatic) leading to its formulation as **7**. The endo geometry of the ether bridge in **7** is deduced from the steric considerations as well as exceptional shielding (τ 9.51) of the C_8-methyl group due to the diamagnetic anisotropy of the phenyl ring. The acetylene **3** could also be trapped with tetracyclone **8** to

(1) (a) A. Krebs in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, p 987; (b) R. W. Hoffman, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, p 317.

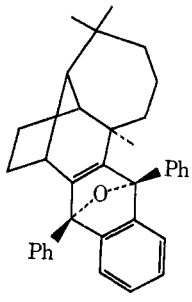
(2) G. Kobrich, *Angew. Chem. Int. Ed. Engl.*, 49 (1965); G. Kobrich and P. Buck, ref 1b, p 99.

(3) M. M. Mehra, B. B. Ghatge, and S. C. Bhattacharyya, *Tetrahedron*, **21**, 637 (1965).

(4) U. R. Nayak, T. S. S. Krishnan, and S. Dev, *ibid.*, **19**, 2281 (1963); S. Ranganathan, A. Goel, and B. B. Singh, *Tetrahedron Lett.*, 3299 (1968).

(5) Private communication from Professor G. Ourisson. We wish to thank Professor Ourisson for this information and a sample of ω-bromolongifolene.

furnish an adduct which after the loss of carbon monoxide gave **9**, mp 261–262°, in 90% yield. The reaction of



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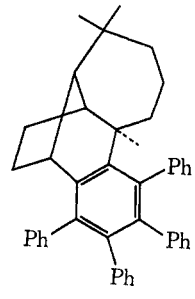

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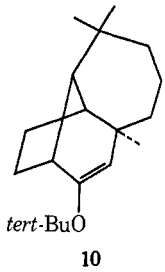
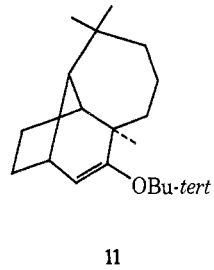
ω-bromolongifolene (**2**) with potassium *tert*-butoxide in the absence of any trapping agent furnished a high yield of a mixture containing ketones **4** and **5** and the *tert*-butyl enol ethers **10** and **11**. The formation of



10



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these compounds is compatible with the formation of **3**. No dimeric products as reported[3] earlier were encountered in this reaction. Mechanistically, this base-induced rearrangement can be visualized as proceeding either *via* an alkylidene carbene[6] or an α-halogenoorganometallic intermediate.[2]

Experimental Section[7]

ω-Bromolongifolene[8] (2).—A solution of longifolene (**1**) (20.4 g, 0.1 mol) and *N*-bromosuccinimide (18 g, 0.1 mol) in dry benzene (150 ml) was refluxed for 4 hr in the presence of a catalytic amount of benzoyl peroxide (100 mg). The reaction mixture was poured into water and the organic layer was successively washed with dilute HCl (10%, three 50-ml portions, saturared $NaHCO_3$ (two 40-ml portions), and brine (two 25-ml portions) and dried. Removal of solvent and distillation gave ω-bromolongifolene: 20 g (72%); mp 40–41°; ir (neat) 3010, 1640, 790 cm^{-1} ($>C{=}C<^{H}$); nmr τ 9.04 (6 H, s, gem Me), 8.95 (3 H, s, Me), 4.37 (1 H, s, olefinic), 6.87 (1 H, broad, allylic bridgehead).

Diphenylisobenzofuran Adduct 7 of Acetylene 3.—A mixture of ω-bromologifolene (**3**) (2.8 g, 0.01 mol), potassium *tert*-butoxide (2.16, 0.2 mol), and diphenylisobenzofuran (**6**) (2.7 g, 0.1 mol) was refluxed in dry toluene for 8 hr. The reaction mixture was diluted with water and extracted with CH_2Cl_2 (two 50-ml portions). The organic phase was washed with brine and freed of solvent to give a solid residue, 4.5 g, mp 249–255°. Recrystallization from methanol gave colorless needles: mp 254–256°; ir spectrum 1655, 1603, 701, 690 (aromatic), 1210 cm^{-1} (ether). *Anal.* Calcd for $C_{35}H_{36}O$: C, 88.94; H, 7.68. Found: C, 88.73; H, 7.61.

Tetracyclone Adduct 9 of Acetylene 3.—A mixture of ω-bromolongifolene (2.80 g, 0.1 mol), tetracyclone (3.84, 0.1 mol), and potassium *tert*-butoxide (2.16 g, 0.2 mol) was refluxed in toluene until the color of tetracyclone was completely discharged (6 hr). The reaction mixture was poured into water and extracted with CH_2Cl_2 (two 60-ml portions). Removal of solvent gave a solid residue. Recrystallization from MeOH–C_6H_6 gave colorless crystals: mp 260–262° (90% yield); ir spectrum 695, 1480, 1601 and 3080 cm^{-1}. *Anal.* Calcd for $C_{43}H_{42}$: C, 92.42; H, 7.58. Found: C, 92.13; H, 7.51.

Rearrangement of 2 with Potassium *tert*-Butoxide.—A mixture of ω-bromolongifolene (5.6 g, 0.2 mol) and potassium *tert*-butoxide (7.3 g, 0.4 mol) in toluene was refluxed for 6 hr. The reaction mixture was poured into water and extracted with pentane (three 50-ml portions), washed with brine, dried, and freed of solvent to yield a pale yellow liquid, 4.13 g. A vpc analysis of the product showed the presence of at least seven components. The major components were in the ratio[10] of 1:5:1:2 and were identified as longihomocamphenilone[3,11] (**4**, mp 55–56°), longiisohomocamphenolone[3] (**5**, mp 51–52°), *tert*-butyl enol ether **10** [bp 140–150° (1 mm); ir spectrum 1645, 1170, 1195, 1240 cm^{-1} (enol ether). *Anal.* Calcd for $C_{19}H_{32}O$: C, 82.54; H, 11.66. Found: C, 82.21; H, 11.51], and the isomeric *tert*-butyl enol ether **11** [bp 140–145° (1 mm); ir spectrum 1650, 1170, 1190, 1240 cm^{-1} (enol ether). *Anal.* Calcd for $C_{19}H_{32}O$: C, 82.54; H, 11.66. Found: C, 82.31; H, 11.59]. The two *tert*-butyl enol ethers were characterized by converting them into the 2,4-dinitrophenylhydrazones of the corrsponding ketones **4**, mp 144°, and **5**, mp 164–165°, by reaction with Brady[12] reagent.

Registry No.—**2**, 1139-15-7; **4** 2,4-DNP, 1607-92-7; **5** 2,4-DNP, 1174-81-8; **7**, 31024-76-7; **9**, 31024-77-8; **10**, 31024-78-9; **11**, 31024-79-0.

(6) K. L. Erickson and J. Wolinsky, *J. Amer. Chem. Soc.*, **87**, 1142 (1965).

(7) Melting points and boiling points are uncorrected. All solvent extracts were dried over anhydrous Na_2SO_4. Ir spectra were recorded on a Perkin-Elmer Model 137 infracord as neat liquids or solids as KBr disks. Nmr spectra were recorded on a Varian A-60 spectrometer in $CDCl_3$ and chemical shifts are reported on a τ scale relative to tetramethylsilane (τ 10).

(8) The reported[9] preparation of **2** involved a two-step bromination–dehydrobromination of longifolene (**1**) and is less convenient.

(9) G. Dupont, R. Dulou, P. Naffa, and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1075 (1954).

(10) The relative amount of the components varied in every reaction with time and the sample of the base used.

(11) P. Naffa and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1115 (1954).

(12) O. L. Brady, *J. Chem. Soc.*, 756 (1931); J. Wolinsky, *J. Org. Chem.*, **26**, 705 (1961).

The Chemistry of Actinobolin. Oxidation of Actinobolamine

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Aromatization of cyclic portions of actinobolin[2,3] and of the products isolated after base-catalyzed[4,5] hydrolysis of the antibiotic made secure the molecular structures assigned to these compounds. Actinobolamine (**1a**),[5] the product formed by vigorous acid hydrolysis of actinobolin, resisted all attempts at achieving clean eliminative scission of the bond linking C-5 to nitrogen and subsequent aromatization of the substituted cyclohexenone. *N*-Acetylactinobolamine (**1b**) did, however, submit to nitric acid oxidation affording a readily isolable product displaying ir bands characteristic of lactone carbonyl. This observation

(1) (a) Support of this work by the National Institutes of Health through Research Grant AI-04720 is gratefully acknowledged. (b) This paper is based in part on the Ph.D. dissertation of D. B. Nelson, Arizona State University. (c) Presented at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, ORGN 014.

(2) M. E. Munk, D. B. Nelson, F. J. Antosz, D. L. Herald, Jr., and T. H. Haskell, *J. Amer. Chem. Soc.*, **90**, 1087 (1968).

(3) F. J. Antosz, D. B. Nelson, D. L. Herald, Jr., and M. E. Munk, *ibid.*, **92**, 4933 (1970).

(4) D. B. Nelson, M. E. Munk, K. B. Gash, and D. L. Herald, Jr., *J. Org. Chem.*, **34**, 3800 (1969).

(5) D. B. Nelson and M. E. Munk, *ibid.*, **35**, 3832 (1970).