viously reported C[4] medium[1] supplemented with 56% $^{13}CH_3CH_2CO_2Na$ (100 mg/40 ml) yielded after a 24-hr incubation isotopically enriched piericidin A. In the nmr spectrum of piericidin A, the C_{14}, C_{15}, C_{16}, C_{17}, and C_{18} methyl resonances are resolved and their positions can be assigned,[2c] thereby allowing most of their corresponding satellites in the labeled compound to be readily located and identified, and their intensities measured. The source of the methoxyl groups in the antibiotic was determined by additional experiments with 56% enriched [$^{13}CH_3$]-methionine (100 mg/40 ml). The nmr data for the labeled piericidins are summarized in Table I.

TABLE I

NMR DATA FOR PIERICIDIN A

			—100-MHz yield[a]—		—60-MHz yield—	
	τ	J^{13}_{CH}, Hz	Upfield satellite	Downfield satellite	Upfield satellite	Downfield satellite
			^{13}C-Propionate			
C_{14} CH_3	8.20	126	8.7[b]	10.1[c]	*d*	*e*
C_{15} CH_3	8.36	124	*d*	10.5[c]	9.8	*e*
C_{16} CH_3	9.18	128	9.6	*f*	12.4	*d*
C_{17} CH_3	8.24	126	7.3[b]	10.5[c]	*e*	*e*
C_{18} CH_3	7.90	130	9.1[g]	*e*	10.2	8.7
			^{13}C-Methionine			
C_{19} OCH_3	6.04	147	15.3	17.3		
C_{20} OCH_3	6.14	146	17.2	17.2		

[a] The yields are expressed a atom per cent excess ^{13}C. The incorporation yields were determined by comparing the area of the satellite peak with the area of the unlabeled carbon-1 methylene protons as an internal standard. Yields represent the area determined *via* a single scan on the Varian HA-100 and A-60A, respectively. Incorporation values are ±15% error. [b] This is an approximate value, since an impurity peak gives an overlapping signal at τ 8.75. [c] Spin decoupling proved that the C_9 proton which appears in this region of the spectrum, does not overlap with this downfield satellite peak. [d] This satellite signal was observed; however, owing to an impurity signal and/or overlapping signals, this yield was not calculated. [e] This satellite signal was completely obscured by overlapping signals. [f] This downfield satellite signal overlapped the upfield satellite signal of the C_{18} CH_3 group. [g] This signal appeared at τ 8.6 together with the C_{16} CH_3 downfield signal. This yield was approximated by subtracting the upfield C_{16} CH_3 area from the total peak area.

These data unequivocally show that five C-methyl groups are biosynthetically derived from the methyl group of propionate and the terminal C_{13} methyl group is not propionate derived. The nearly equal labelling pattern observed in the methyl groups along the chain implies that only a single polyketide chain is assembled subsequent to nitrogen introduction to form the pyridine ring. No other biogenetic unit appears to be involved. These results amplify and are in accord with the ^{14}C biosynthesis work.

We observed that incorporation of [$^{13}CH_3$]-methylmalonic acid into piericidin A was very low, since satellite bands could not be observed with a single scan. The poor incorporation is probably due to a cell membrane permeability effect. A similar result was observed in the biosynthesis of erythromycin.[5]

The general use of $^{13}CH_3CH_2CO_2Na$ and nmr for establishing the origin of methyl groups derived from propionate in microbial metabolites is a useful technique and high incorporation yields can be generally anticipated. The method is a useful complement to the radio carbon method.

(5) S. M. Friedman, T. Kaneda, and J. W. Corcoran, *J. Biol. Chem.*, **239**, 2396 (1964).

Registry No.—Piericidin A, 24467-35-4.

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Diels–Alder Reaction of Tetrachloroethylene with Anthracene

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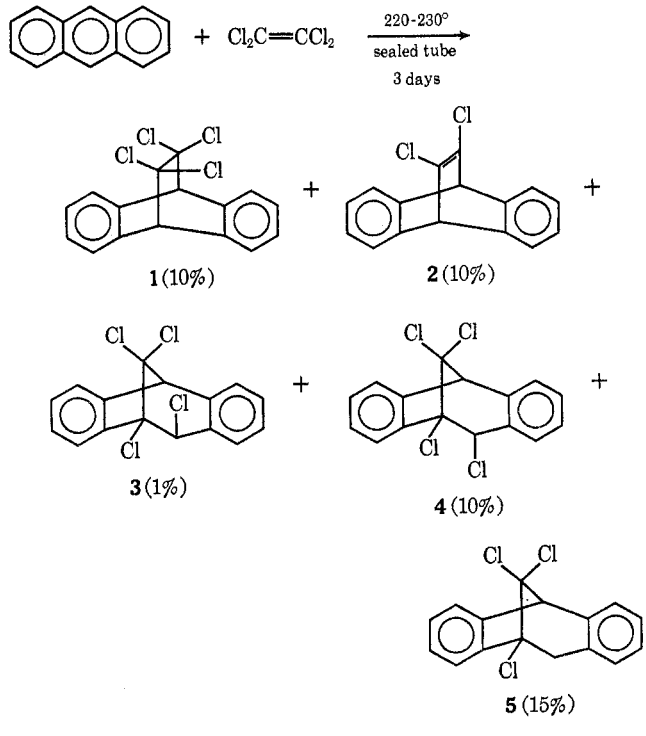
In connection with other experiments we wished to synthesize 11,11,12,12-tetrachloro-9,10-dihydro-9,10-ethanoanthracene (**1**). The only mention in the literature of this compound is the report of Russian workers[1,2] that **1** results from the Diels–Alder reaction of tetrachloroethylene with anthracene. We have repeated



this reaction and find that indeed **1** (mp 205–206°) is produced, albeit in a mixture with a number of other compounds. One of these other characterizable products is 11,12-dichloro-9,10-dihydro-9,10-ethenoanthracene (**2**), which from the melting point (179–180°) appears to be the compound the earlier workers assigned as **1**. The conclusion is supported by dipole-

(1) V. M. Zonoastrova and B. A. Arbuzov, *Dokl. Akad. Nauk SSSR*, **60**, 59 (1948).

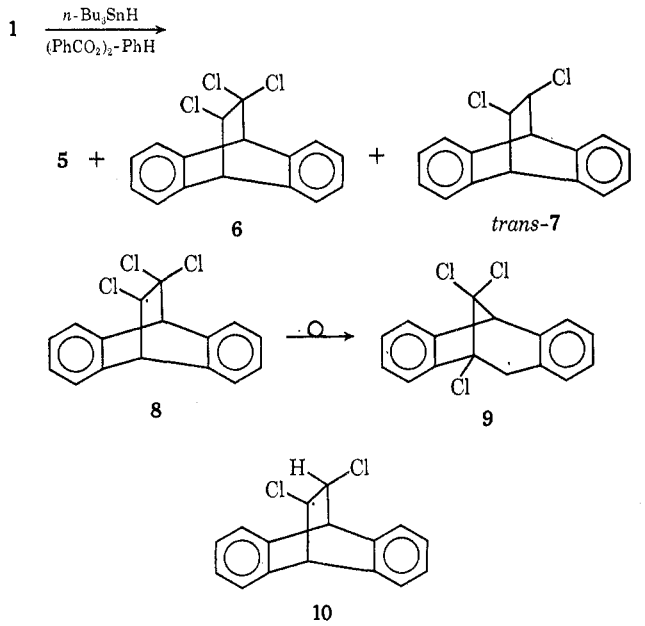
(2) B. A. Arbuzov and A. N. Vereshchagin, *Bull. Acad. Sci. USSR*, 936 (1964).

moment studies[2] on the compound isolated by the Russians; the observed dipole moment for the Russians' compound (mp 178–180°) is 2.09 D, a value more in agreement with structure **2**.

The Diels–Alder reaction of tetrachloroethylene and anthracene yields three other compounds in addition to **1** and **2** plus large amounts of tars. Compounds **3** and **4** were synthesized in high yields from the ionic addition of chlorine to **2** in nitromethane (**3** isomerizes to **4** when allowed to stand under these reaction conditions for longer periods of time; similar isomerizations have been observed previously)[3] while the free-radical addition of chlorine to **2** in carbon tetrachloride gives **1** in quantitative yield.[4] Treatment of **3** and/or **4** with hydrogen in the presence of 10% Pd–C converts these compounds to **5**.

If the Diels–Alder reaction is run at 210° for 2 days, one obtains the normal addition product **1** with only small amounts of side products; however, the reaction occurs only to a small extent, and large amounts of unreacted anthracene result. When the tetrachloride **1** is heated (neat) in a sealed tube at 230° for 1 day, it is partially converted to **4**. (When **3** is heated under these conditions, it is >90% converted to **4**.) If this reaction is run in the presence of anthracene, **5** also is observed among the products. What appears to be happening is that **1** loses chlorine at high temperature to give **2** which then undergoes ionic addition of chlorine to give the rearranged chlorides **3** and **4**. In the presence of anthracene, chlorine reacts to give 9,10-dichloro-9,10-dihydroanthracene which would be expected to lose hydrogen chloride readily (accounting for the hydrogen chloride observed in this reaction; see Experimental Section) to give 9-chloroanthracene.[6] 9,10-Dichloro-9,10-dihydroanthracene might also act as a source of hydrogen atoms for the reduction of **3** and/or **4** to **5**. We have tested this by heating a mixture of **3** and **4** with 9,10-dihydroanthracene (230°, 1 day) and find that **3** and **4** are completely hydrogenolyzed to **5**. Similar treatment of the tetrachloride **1** with 9,10-dihydroanthracene apparently also gives **5**, but this reaction yields a large number of unidentifiable products.

The trichloride **5** also is produced in the reaction of **1** with tri-*n*-butyltin hydride (*n*-Bu_3SnH) in refluxing benzene, a type of reaction known[7] to proceed *via* a free-radical mechanism. The relative amount of **5** increases with increasing dilution of *n*-Bu_3SnH, a fact consistent with a rearrangement[8] of radical **8** to the more stable benzylic radical **9** followed by chain transfer with *n*-Bu_3SnH to give **5**. Reduction of **1** with a relatively high concentration of *n*-Bu_3SnH yields only **6**. When **6** is allowed to react with *n*-Bu_3SnH under these conditions, only *trans*-**7** results, and no products arising from rearrangement are observed even at high dilution. The fact that **8** rearranges while the radical **10** does not is probably due to the increased steric inhibition to chain transfer caused by the presence of two β-chlorine atoms in radical **8** compared with only one β-chlorine atom in radical **10**.[9]



Experimental Section[13]

Preparation of 11,11,12,12-Tetrachloro-9,10-dihydro-9,10-ethanoanthracene (1) by Diels–Alder Reaction with Anthracene.—Into a 26-in. thick-walled glass tube were placed 20 g (0.11 mol) of purified anthracene, 70 ml of tetrachloroethylene (0.683 mol), and 0.5 g of 4-*t*-butylpyrocatechol. The sealed tube was placed in a heater for 2.5 days with the temperature maintained at 220–230°. *Caution:* Upon opening there may be pressure due to HCl gas. The reaction solution was transferred to a 500-ml round-bottom flask with methylene chloride and the volatile solvents were removed by rotary evaporation. To the round-bottom flask were added 15.0 g (0.153 mol) of maleic anhydride and 100 ml of *p*-xylene. The mixture was stirred at reflux for 4 hr after which the warm solution was filtered and the *p*-xylene removed by rotary evaporation. The resulting crude product was taken up in 200 ml of ether and extracted twice with 100-ml portions of saturated sodium carbonate solution. The ether layer was dried over magnesium sulfate and the ether removed by rotary evaporation to give 18 g of crude oil.

The crude product was placed, using a minimum amount of carbon tetrachloride, on a 5-ft chromatography column containing 400 g of Fischer silica gel. The column was eluted with 5% benzene–95% Skellysolve B. First off the column was **2** (3 g, 10%), mp 179–180°,[5] followed by a mixture of **1** (3.8 g, 10%), mp 204–205°, *endo*-4-chloro-5,8,8-trichlorodibenzobicyclo[3.2.1]-octadiene (**4**) (3.4 g, 10%), mp 135–136°, and 5,8,8-trichlorodibenzobicyclo[3.2.1]octadiene (**5**) (4.5 g, 15%), mp 124–125°. There were traces of *exo*-4-chloro-5,8,8-trichlorodibenzobicyclo-[3.2.1]octadiene (**3**) (*ca.* 1%), mp 147–148.5°, in the last fractions

(3) S. J. Cristol and B. B. Jarvis, *J. Amer. Chem. Soc.*, **88**, 3091 (1966).

(4) This in fact proves to be the best procedure for obtaining **1** or **3** and **4**, since **2** can be made in high yield from 11,11,12-trichloroethanoanthracene by treatment with potassium *t*-butoxide in dimethyl sulfoxide.[5]

(5) B. B. Jarvis, Ph.D. Thesis, University of Colorado, 1966.

(6) Careful work-up of this reaction mixture does indeed yield a small amount (isolated by glpc) of 9-chloroanthracene.

(7) D. J. Carlsson and K. V. Ingold, *J. Amer. Chem. Soc.*, **90**, 7047 (1968).

(8) C. Walling in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963 Chapter 7.

(9) Free-radical phenyl migrations seldom have been observed in bridged bicyclic systems.[10] A number of free-radical additions to 9,10-dihydro-9,10-ethenoanthranes have been reported,[11,12] but no products arising from free-radical rearrangements were observed. We have investigated the free-radical additions of carbon tetrahalides to a number of 11-substituted 9,10-dihydro-9,10-ethenoanthracenes and find that extensive rearrangements of the intermediate radicals do occur and in a rather stereoselective manner. These results will be reported shortly.

(10) S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3727 (1967).

(11) S. J. Cristol, R. Caple, R. M. Sequeira, and L. O. Smith, Jr., *J. Amer. Chem. Soc.*, **87**, 5679 (1965).

(12) B. B. Jarvis, *J. Org. Chem.*, **33**, 4075 (1968).

(13) Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Proton magnetic resonance spectra were measured in carbon tetrachloride solutions with a Varian A-60D pmr spectrometer with tetramethylsilane (τ 10.00) as an internal standard. Infrared spectra were measured in carbon tetrachloride solution on a Beckman IR-8 infrared spectrometer. Elemental analyses were performed by Dr. F. J. Kasler, University of Maryland.

collected. All fractions were weighed and analyzed by thin layer chromatography, pmr spectra, and ir spectra. All the above products except **3** were isolated and their structures characterized by pmr and ir spectra, melting points, and carbon–hydrogen analyses.

Outside the aromatic region, the pmr spectra show (a) for **1** a singlet (2 H) at τ 5.14, (b) for **2** ($\nu_{C=C}$ at 1600 cm^{-1}) a singlet (2 H) at τ 5.03, (c) for **3** two singlets (1 H each) at τ 5.43 and 4.61, (d) for **4** two singlets (1 H each) at τ 5.44 and 4.31, (e) for **5** a singlet (1 H) at τ 5.44 and a pair of doublets (1 H each, J_{gem} = 16.5 Hz) at τ 6.67 and 6.18.

Anal. Calcd for $C_{16}H_{10}Cl_4$ (**1**): C, 55.85; H, 2.93. Found: C, 55.58; H, 3.03. Calcd for $C_{16}H_{10}Cl_4$ (**3**): C, 55.85; H, 2.93. Found: C, 55.87; H, 3.09. Calcd for $C_{16}H_{10}Cl_4$ (**4**): C, 55.85; H, 2.93. Found: C, 55.83; H, 3.05. Calcd for $C_{16}H_{11}Cl_3$ (**5**): C, 62.07; H, 3.58. Found: C, 62.09; H, 3.65.

A similar reaction of anthracene with tetrachloroethylene in a sealed tube at 210° for 2 days gave large amounts of recovered anthracene (*ca.* 80% recovery). Anthracene was separated from the crude reaction mixture (*via* crystallization and the formation of the maleic anhydride adduct of anthracene), and a pmr spectrum of the resulting mixture showed the presence of **1** with only trace amounts of other products. Chromatography over alumina gave **1** in *ca.* 5% yield.

Preparation of 3 and 4.—Dry chlorine gas was bubbled into a stirred solution of 10.0 g (36.6 mmol) of **2** in 50 ml of nitromethane until saturation was achieved. The reaction vessel was stoppered and wrapped in aluminum foil to prevent photoinitiated reactions from taking place. The reaction progress was followed by the disappearance of the double-bond absorption (1600-cm^{-1} band) in the ir spectrum. After standing at room temperature for 1 day, a 50:50 mixture (by pmr spectroscopy) of the two epimers **3** and **4** resulted. The crude product, 7.5 g of oil, was crystallized from ethanol to give 2.0 g (16% yield) of each epimer. The low yield was due to the difficulty involved in separating the two epimers. The epimers could also be separated by chromatography over silica gel (**4** is eluted first with 5% benzene in Skellysolve B).

Photochlorination of 2 to Give 1.—Dry chlorine gas was bubbled through a solution of 1.0 g (3.36 mmol) of **2** in 20 ml of carbon tetrachloride until the solution turned deep green. The reaction vessel was stoppered and set in the presence of a sun lamp for 5 hr, after which time the double bond absorption at the 1600-cm^{-1} band in the ir spectrum had disappeared. The carbon tetrachloride was removed by rotary evaporation and the remaining oil crystallized from Skellysolve B to give 1.1 g (87% yield) of **1**, mp 204–205°.

Preparation of 5.—The reaction vessel containing 3.0 g (8.7 mmol) of a 50:50 mixture of **3** and **4** in 50 ml of ethanol was placed in a Parr bomb hydrogenation apparatus and flushed several times with hydrogen gas. The mixture was allowed to react for 2.5 days at 40-psi hydrogen gas pressure. The catalyst was removed by filtration, and the ethanol was removed by rotatary evaporation to give an oil which was crystallized from methanol to give 1.0 g (35%) of 5,8,8-trichlorodibenzobicyclo-[3.2.1]octadiene (**5**), mp 124–125°.

Treatment of 1 and 3 and 4, under Diels–Alder Reaction Conditions.—In 0.5-in. medium-walled glass tubes were sealed (a) 0.35 g of **1**, (b) 0.38 g of **1** and 0.51 g of anthracene, (c) 0.43 g of a mixture of **3** (90%) and **4** (10%) and 0.25 g of 9,10-dihydroanthracene, and (d) 0.31 g of **1** and 0.28 g of 9,10-dihydroanthracene. These tubes were heated at 230° in a silicon oil bath for 1 day. The tubes were opened, and pmr spectra were taken of the resulting dark colored mixtures.

(a) The pmr spectrum showed **1** and **4** present in the ratio of 2:1, respectively. A trace of **3** also was discernible in the pmr spectrum. Isolation by chromatography gave 0.19 g (54%) of recovered **1** and 0.10 g (29%) of **4**.

(b) The pmr spectrum indicated the presence of **1**, **4**, and **5** but in admixture with a number of unidentifiable compounds. This mixture was worked up by chromatography over silica gel. The fractions containing anthracene were combined and analyzed by glpc [5-ft column with 20% SE-30 on Chromosorb W (60–80 mesh) at 200°]. The peak that corresponded to 9-chloroanthracene (ratio of anthracene to 9-chloroanthracene was *ca.* 20:1) was collected and shown to be 9-chloroanthracene by ir and mixture melting point with an authentic sample of 9-chloroanthracene.[14]

(14) D. C. Nonhebel, *J. Chem. Soc.*, 1216 (1963).

(c) The pmr spectrum showed only anthracene and **5** present. These were separated by chromatography over silica gel to give 0.25 g (65%) of **5**.

(d) The pmr spectrum was similar to that of reaction b. No attempt was made to isolate the products.

Reduction of 1 with Tri-*n*-butyltin Hydride (Dilute Conditions).—To a solution of 0.5 g (1.45 mmol) of **1** in 50 ml of dry benzene at reflux was slowly added (under nitrogen) a solution of 0.411 g (1.42 mmol) of tri-*n*-butyltin hydride and 40 mg of benzoyl peroxide dissolved in 30 ml of dry benzene. Reflux was maintained for 14 hr. A pmr spectrum was taken which indicated the presence of **1** (10%), **6** (32%), **2** (*ca.* 1%), **7**[15] (15%), and **5** (42%). The solvent was removed and the oil placed on a chromatography column containing 25 g of Fischer absorption alumina. The column was eluted with 3% benzene–97% Skellysolve B. Partial separation was achieved by this method. First off the column was a mixture of **2** and **5** followed by **2** and then a second mixture of **1** and **6**. The fractions collected were analyzed by thin layer chromatography and pmr spectroscopy.

Reduction of 1 with Tri-*n*-butyltin Hydride (Concentrated Conditions).—A solution of 30 ml of dry benzene, 0.50 g (1.45 mmol) of **1**, 0.67 g (2.3 mmol) of *n*-BuSnH, and 40 mg of benzoyl peroxide were held at reflux (under nitrogen). After 11 hr at reflux the solution was concentrated, and a pmr spectrum indicated the presence of *n*-Bu_3SnCl and a mixture of **6**[1] (80%) and **7**[12] (20%).

Reduction of 6 with Tri-*n*-butyltin Hydride.—Similar treatment of **6** with *n*-Bu_3SnH either at high or low concentrations gave **7** as the only observable product.

Registry No.—Tetrachloroethylene, 127-18-4; anthracene, 120-12-7; **1**, 17189-63-8; **3**, 24162-33-2; **4**, 24118-59-0; **5**, 24118-60-3; **2**, 24162-34-3.

Acknowledgment.—We wish to thank the donors of the Petroleum Research Fund administered by the American Chemical Society for support of this work.

(15) S. J. Cristol and N. L. House, *J. Amer. Chem. Soc.*, **74**, 2193 (1952).

Halogenation with Copper(II) Halides. Synthesis of Copper(I) Bromide–Diolefin Complexes

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Copper(I) halide–olefin complexes have been prepared by treatment of an ethanolic solution of copper(II) halide and olefin with sulfur dioxide.[1] This technique, which is dependent upon the reduction of copper(II) to copper(I) by sulfur dioxide, has been utilized for the preparation of both copper(I) chloride– and bromide–olefin complexes. The synthesis of two copper(I) bromide–olefin complexes has been described in which the presence of a reducing agent was not required. The addition of norbornadiene[2] or *cis,trans*-cyclodeca-1,5-diene[1c] to a solution of copper(II) bromide dihydrate in ethanol led directly to the formation and precipitation of the corresponding copper(I) bromide complexes. While it was apparent that a redox reac-

(1) (a) H. L. Haight, J. R. Doyle, N. C. Baenziger, and G. F. Richards, *Inorg. Chem.*, **2**, 1301 (1963); (b) J. H. van den Hende and W. C. Baird, Jr., *J. Amer. Chem. Soc.*, **85**, 1009 (1963); (c) J. C. Trebellas, J. R. Olechowski, and H. B. Jonassen, *Inorg. Chem.*, **4**, 1818 (1965).

(2) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).