After two recrystallizations from a benzene–*n*-hexane mixture, the colorless crystals had mp 112–113° and infrared absorptions (KBr disk) at 5.75 (ester C=O) and 6.00 μ (amide C=O).

Anal. Calcd for $C_{10}H_{15}O_3N$: C, 60.89; H, 7.67; N, 7.10. Found: C, 60.93; H, 7.65; N, 7.05.

Methyl 4-(N-Carbomethoxy)aminobicyclo[2.2.1]heptane-1-carboxylate (6).—A mixture of 1.6 g (0.0081 mole) of amide **5** and 32 ml of a solution of 0.64 g of sodium in 48 ml of methanol (0.019 g-atom of sodium) was cooled in an ice–salt bath. The solution was stirred magnetically while 2.9 ml of a solution of 0.9 ml of bromine in 4.1 ml of methanol (0.012 mole bromine) was added dropwise for 3 hr. Stirring was maintained for another 5 hr, during which period the ice had melted and the mixture had become room temperature. The mixture was poured over 200 ml of water, the water extracted with hexane, and the hexane solution dried over magnesium sulfate. After evaporation of the hexane, a colorless oil was obtained. An attempt to crystallize this oil failed. The infrared absorption spectrum (liquid film), with maxima at 5.8, 5.9 (C=O) and 6.55 μ (N–H), of the crude product supported the proposed structure, and the urethan was used for the next preparation without purification.

4-Aminobicyclo[2.2.1]heptane-1-carboxylic Acid Hydriodide (7).—A mixture of the urethan, **6**, obtained from 1.6 g (0.0081 mole) of amide and 7 ml of hydriodic acid (analytical reagent grade) in a 25-ml round-bottomed flask was heated in an oil bath at 100° for 6 hr and allowed to stand overnight. The excess hydriodic acid was removed on a flash evaporator. The residue was dried *in vacuo* at room temperature and washed with two small portions of acetone. Filtration gave 1.2 g of the acid hydriodide (52%, based upon the amide **5**). After recrystallization from ethanol–ethyl acetate mixture, the product (mp 270° dec) was obtained. The infrared absorption spectrum (KBr disk) showed a strong peak at 5.86 (C=O) and broad complex peaks at 2.8–4 μ (acid OH). The acid hydriodide was used without further purification.

4-Carbomethoxybicyclo[2.2.1]heptane-1-trimethylammonium Iodide (8).—A solution of 0.15 g (0.00053 mole) of the acid hydriodide **7**, 0.11 ml (0.0018 mole) of methyl iodide, 0.15 g (0.0018 mole) of sodium bicarbonate, and 6 ml of methanol was heated under reflux for 70 hr. At the end of 24 and 48 hr, 0.5 ml of methyl iodide was added. The excess methyl iodide and methanol were evaporated on a steam bath and the residue was extracted with six 10-ml portions of boiling chloroform. The chloroform was evaporated and the residue recrystallized from ethanol. The colorless crystals (0.13 g, 72%), mp 240°, had infrared absorption (KBr disk) at 5.78 μ (C=O). An nmr spectrum showed peaks at τ 7.75–8.20 (complex multiplet, 10 H), 6.9 (singlet, 9 H), and 6.40 (singlet, 3 H).

Anal. Calcd for $C_{12}H_{22}NO_2I$: C, 42.48; H, 6.59; N, 4.13; I, 37.41. Found: C, 42.67; H, 6.66; N, 4.20; I, 37.63.

4-Carboxybicyclo[2.2.1]heptane-1-trimethylammonium Iodide (9).—A solution of 4-carbomethoxybicyclo[2.2.1]heptane-1-trimethylammonium iodide (0.5 g, 0.0015 mole) and 3 ml of 1 *N* hydriodic acid was heated in a sealed tube at 100° for 10 hr. After the mixture was cooled and filtered, 0.35 g (73%) of the product **9** was isolated. Recrystallization from absolute ethanol yielded colorless crystals, mp 265° dec. The infrared spectrum (KBr disk) showed carbonyl absorption at 5.80 μ. The nmr spectrum showed peaks at τ 7.75–8.2 (multiplet, 10 H), 6.9 (singlet, 9 H), and 5.5 (singlet, 1 H).

Anal. Calcd for $C_{11}H_{20}NO_2I$: C, 40.63; H, 6.20; N, 4.31; I, 39.03. Found: C, 40.50; H, 6.05; N, 4.45; I, 39.24.

Methyl 4-Cyanobicyclo[2.2.1]heptane-1-carboxylate (10).—A solution of amide ester **5** (0.3 g, 0.0015 mole), 5 ml of ethylene dichloride, and 0.5 ml of phosphorus oxychloride was refluxed on a steam bath for 20 min. The solvent and excess phosphorus oxychloride were removed under slightly reduced pressure. The residue was treated with ice-cold 2 *N* sodium hydroxide and then extracted with *n*-pentane. The *n*-pentane solution was washed with water and dried over magnesium sulfate. After the *n*-pentane was removed *ca.* 0.2 g of a colorless oil was obtained and used for the next preparation without purification. The infrared absorption spectrum (liquid film) showed maxima at 4.43 (C≡N) and 5.75 μ (C=O).

4-Cyanobicyclo[2.2.1]heptane-1-carboxylic Acid (11).—A solution of cyano ester **10** prepared from the preceding reaction, 0.7 ml of 0.8 *N* KOH in 87% methanol, and 4 ml of 87% methanol was refluxed for 1 hr. The solution was cooled, diluted with 15 ml of water, washed with ether to remove the starting cyano ester saturated with sodium chloride, acidified with 6 *N* hydrochloric acid, and finally extracted with ether. The ether solution after drying over magnesium sulfate was evaporated and the product crystallized from an ether–*n*-hexane mixture. The colorless crystals (0.18 g, 73%, based upon the amide ester), mp 137°, had infrared absorptions (KBr disk) at 4.43 (C=N) and 5.90 μ (C=O). The nmr spectrum (perdeuterioacetone) showed absorptions at τ 5.33 (broad singlet, 1 H) and 7.6–8.3 (complex multiplet, 10 H).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.48. Found: C, 65.26; H, 6.79; N, 8.31.

Methyl 4-Bromobicyclo[2.2.1]heptane-1-carboxylate (12).—A solution of bromine (0.4 ml, 0.0075 mole) in 6 ml of bromotrichloromethane in a 50-ml, three-necked flask fitted with magnetic stirrer, reflux condenser, and dropping funnel was heated to 45° in an oil bath. A slurry of half-ester **4** (0.7 g, 0.0035 mole), mercuric oxide (0.5 g, 0.0023 mole), and 20 ml of bromotrichloromethane in a 50-ml addition funnel was added dropwise to the reaction flask with vigorous stirring. After the addition was completed, the temperature of the oil bath was maintained at 70° for 1 hr. The mixture was cooled and filtered. The filtrate was washed with aqueous sodium thiosulfate and potassium hydroxide solution and dried over calcium sulfate. The solvent was removed under reduced pressure. The infrared absorption spectrum (KBr disk) of the crude product showed a single carbonyl band at 5.76 μ. The nmr spectrum showed peaks at τ 7.8–8.4 (complex multiplet, 10 H) and 6.35 (singlet, 3 H).

4-Bromobicyclo[2.2.1]heptane-1-carboxylic Acid (13).—A solution of bromo ester in 10 ml of 48% hydrobromic acid was stirred magnetically in a stoppered 50-ml, round-bottomed flask for 14 hr, and then heated at 67° for 1 hr. After cooling, the mixture was diluted with 20 ml of water and extracted with ether. The ether solution was extracted with aqueous sodium bicarbonate. The aqueous solution was saturated with sodium chloride, acidified with hydrobromic acid, and then extracted with ether. This ether solution was dried over magnesium sulfate and then evaporated. Recrystallization of the product from a benzene–hexane mixture yielded 0.4 g of colorless crystals (51%), mp 148°, which sublimed at 85°. The infrared absorption spectrum (KBr disk) showed a maximum at 5.9 μ (C=O), and the nmr spectrum (CCl_4) showed peaks at τ 7.8–8.2 (complex multiplet, 10 H) and −1.4 (broad, 1 H).

Anal. Calcd for $C_8H_{11}O_2Br$: C, 43.86; H, 5.06; Br, 36.48. Found: C, 43.76; H, 5.10; Br, 36.50.

Registry No.—**2**, 15544-51-1; **3**, 15448-76-7; **4**, 15448-77-8; **5**, 15448-78-9; **6**, 15448-79-0; **7**, 15448-80-3; **8**, 15448-81-4; **9**, 15448-82-5; **10**, 15448-83-6; **11**, 15448-86-9; **12**, 15448-84-7; **13**, 15448-85-8.

Dakin–West Reactions on 2-(Purin-6-ylthio)propionic Acid[1]

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In connection with studies on the acylation of various purines,[2] attempts were made to cyclize 2-(purin-6-ylthio)propionic acid (**1**) with acetic anhydride. Ring closure could be expected to occur at the 7- or 1-nitrogen atoms. However, analytical and spectral data showed the compound to be ketone **2**. The presence of the 2-acetyl-2-ethyl group on the sulfur of compound **2** was confirmed by its hydrolysis under mild conditions to compound **3**, which was synthesized from purine-6-thione and 3-chloro-2-butanone in dimethylformamide

(1) This investigation was supported by Public Health Service Research Grant No. CA-03477 from the National Cancer Institute.

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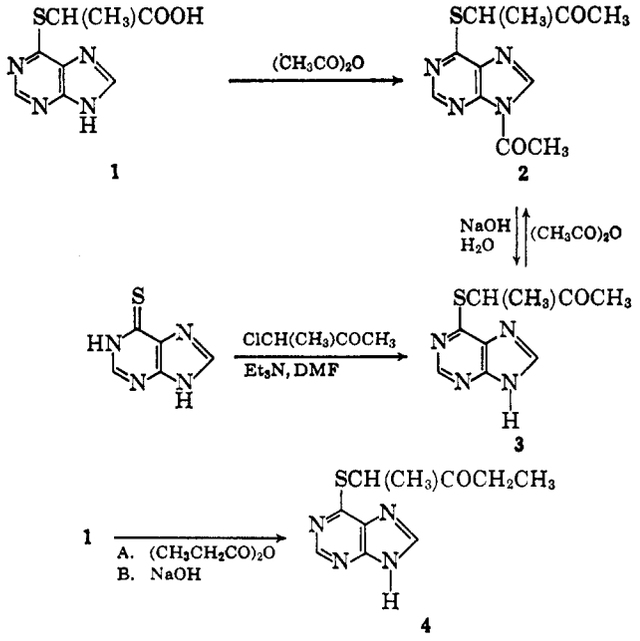


with either potassium carbonate or triethylamine as the acid acceptor. Compound **3** was converted into the acetyl derivative **2** with acetic anhydride.

The acetyl group on nitrogen in compound **2** could be at the 9 or 7 position, but only one isomer was obtained by either synthetic route. The assignment to the 9 position was made on the basis of the expected steric effect of the large group at the 6 position. 6-Methylpurine has been shown[3,4] to react with acetic anhydride exclusively at the 9 position, whereas purine itself gave a mixture of 9- and 7-acetylpurine. The pmr spectrum of the acetylated purine **2** showed a larger shift downfield for the 8 proton (17 cps) than for the 2 proton (9 cps) when compared to the 8 and 2 protons of the unacetylated purine **1**. This is consistent with previous observations[3,4] that acetylation on the imidazole ring has a greater effect on the frequency of the 8 proton than on that of the 2 proton.

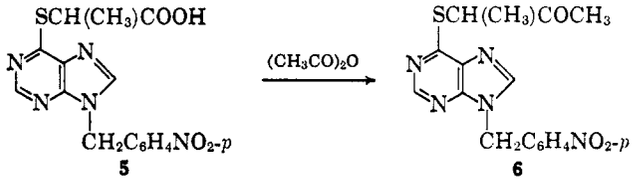
Compound **1** reacted in the same way with propionic anhydride as with acetic anhydride to give, after mild hydrolysis, 6-[2-(3-oxopentylthio)]purine (**4**).

These acylative decarboxylations are examples of the Dakin–West reaction, first observed with amino acids[5] and subsequently shown to occur with a number of other types of compounds.[6] Recently Iwakura and coworkers proved[7] the correctness of the hypothesis[5,8] that 4-acyl-5-oxazolones are intermediates in the amino acid series.

The amino acids and other compounds undergoing acylative decarboxylation have in common an acidic hydrogen and an electron-withdrawing group, both on the α-carbon atom.[6] With the single exception of α-aminophenylacetic acid, these compounds require a basic catalyst, either organic or inorganic.[6] For example, for the conversion of 3-pyridylacetic acid into 3-pyridylacetone[9] and of 2-(3-oxo-2,3-dihydropyridazinyl) acetic acid into 2-(3-oxo-2,3-dihydropyridazinyl) acetone,[10] pyridine or sodium acetate was required as catalyst in spite of the presence of a potentially basic nitrogen in the heterocyclic ring. In the purines currently studied, however, the reaction occurred without the addition of a base. Apparently the S-purinyl group of compound **1** was both sufficiently electrophilic to permit acylation at the α position, and also basic enough to serve as its own catalyst. Moreover, the S-purinyl group was able to overcome the $+I$ effect of the adjacent methyl group which appeared to prevent reaction with α-phenylpropionic acid.[10]

To find out whether the sulfur of the S-purinyl group was a major contributor to the success of the acylative decarboxylation of 2-(purin-6-ylthio)propionic acid, a comparison was made of the reactions of phenoxyacetic acid and of thiophenoxyacetic acid toward acetic anhydride in the presence of pyridine derivatives. There is no previous work on the application of the Dakin–West reaction to acids containing sulfur on the α-carbon atom. The current results showed that thiophenoxyacetic acid did not react in the absence of base, but gave a 21% yield of thiophenoxyacetone in the presence of 2,6-lutidine. Phenoxyacetic acid behaved similarly, yielding phenoxyacetone in 17% yield only in the presence of base (pyridine). A previous investigator reported[11] a yield of 17% of the corresponding ketone from *o*-chlorophenoxyacetic acid and acetic anhydride with pyridine. Hence the purine group rather than the sulfur exerts the chief favorable influence on the reaction.

Alkylation of the imidazole ring of the purine **1** had little effect on the course of the reaction, since 9-*p*-nitrobenzyl-6-[2-(2-carboxyethylthio)]purine (**5**) gave the expected ketone (**6**) in 40% yield on refluxing with acetic anhydride. (The yield of **2** from acetylation of **1** was 57%.)



Experimental Section

Melting points were determined on a Fisher-Johns apparatus and are corrected. The ultraviolet spectra were obtained on a Perkin-Elmer 202 spectrophotometer. The infrared spectra (in potassium bromide) were done on a Perkin-Elmer 337 or 137 spectrophotometer. The pmr spectra (in dimethyl sulfoxide-d_6) were obtained on a Varian A-60A spectrometer using tetramethylsilane as internal standard. Paper chromatographs (descending) were obtained on Whatman No. 1 paper with a mixture of 1-butanol, water, and acetic acid, 45:45:10. The spots were detected with an ultraviolet lamp. Microanalyses were performed by A. Bernhardt, Mülheim (Ruhr), Germany, and by Microanalysis, Inc., Wilmington, Del.

9-Acetyl-6-[2-(3-oxobutylthio)]purine (2).—A suspension of 2-(purin-6-ylthio)propionic acid[12] (1.0 g, 4.40 mmoles) in 30 ml of acetic anhydride was refluxed under anhydrous conditions for 5 hr and the solution then stirred overnight at room temperature. Carbon dioxide evolution was followed in a barium hy-

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droxide trap. Removal of the acetic anhydride *in vacuo* at 50–60° yielded a brown solid which was triturated with 10 ml of ether, dried *in vacuo* over potassium hydroxide at room temperature, and then extracted with nine 40-ml portions of *n*-hexane to give 0.66 g (57%) of crude product, mp 98–99° dec. Recrystallization twice from dry *n*-hexane gave the analytical sample: mp 104–106°; infrared spectrum, carbonyl absorption at 1720 cm^{-1}; pmr spectrum, τ_{max} at 8.49 (doublet 3 H), 7.69 (singlet 3 H), 7.09 (singlet 3 H), 5.08 (quartet 1 H), 1.19 (singlet 1 H), 1.12 (singlet 1 H); λ_{max} ($\epsilon \times 10^{-3}$) in *n*-hexane 283 (14.90).

Anal. Calcd for $C_{11}H_{12}N_4O_2S$: C, 50.00; H, 4.55; N, 21.30; S, 12.10. Found: C, 50.43; H, 4.76; N, 21.12; S, 12.19.

Compound **2** was obtained in 90% yield by acetylation of 6-[2-(3-oxobutylthio)]purine (**3**). A suspension of 0.5 g of **3** in 10 ml of benzene and 2 ml of acetic anhydride gave a clear solution after refluxing for 30–40 min. The product, isolated by the procedure above, was identical with **2**, as shown by mixture melting point and analyses.

6-[2-(3-Oxobutylthio)]purine (3).—To a solution of sodium hydroxide (0.24 g, 6 mmoles) in 40 ml of water, was added 9-acetyl-6-[2-(3-oxobutylthio)]purine (**2**) (1.4 g, 5.3 mmoles). The solid gradually dissolved on heating and stirring for 20 min. The cooled solution was adjusted to a pH of 5 with glacial acetic acid. On refrigeration, a white solid precipitated, 0.9 g (76%), mp 180–183°. Recrystallization from water gave colorless needles: mp 187–189° dec; pmr spectrum, τ_{max} at 8.45 (doublet 3 H), 7.65 (singlet 3 H), 5.02 (quartet 1 H), 1.45 (singlet 1 H), 1.39 (singlet 1 H); λ_{max} ($\epsilon \times 10^{-3}$) in pH 1 304 (15.0), MeOH 284 (11.4), in pH 11 290 (12.2); R_{Ad} 1.69.

Anal. Calcd for $C_9H_{10}N_4OS$: C, 48.63; H, 4.53; N, 25.20. Found: C, 48.64; H, 4.85; N, 24.99.

Compound **3** was also obtained by alkylation of purine-6-thione. A suspension of 2.0 g (11.7 mmoles) of purine-6-thione and 1.18 g (1.64 ml, 11.7 mmoles) of triethylamine in 10 ml of anhydrous dimethylformamide was stirred for 10 min at room temperature under anhydrous conditions. 3-Chloro-2-butanone (1.25 g, 1.21 ml, 11.7 mmoles) was added all at once and the mixture stirred for 15 hr. The mixture was then poured into 40 ml of ice water, and the pH adjusted to 5 with glacial acetic acid. The solid (1.2 g) was collected by filtration and dried at 70°; a second crop (0.6 g) was obtained from the mother liquor (total yield 69%). Recrystallization from water gave the product, mp 186–187° dec, which did not depress the melting point of compound **3**. Compound **3** was also obtained in a poorer yield (42%) by alkylation with potassium carbonate as the base.

6-[2-(3-Oxopentylthio)]purine (4).—A solution of compound **1** (2.0 g, 8.95 mmoles) and propionic anhydride (60 ml) was refluxed under anhydrous conditions for 6 hr. The propionic anhydride was removed *in vacuo* at 60°. The brown residue was triturated with two 10-ml portions of *n*-hexane and dried *in vacuo* over potassium hydroxide at room temperature. Extraction of the tan solid with three 100-ml portions of ether yielded 1.1 g (44%) of the crude acylated material which was not purified further. To a solution of 0.151 g of sodium hydroxide in 25 ml of water was added 0.86 g (2.9 mmoles) of the crude acylated material and the mixture was heated with stirring for 20 min. The resulting solution was cooled, the pH adjusted to 5 with glacial acetic acid, and the precipitate collected and dried *in vacuo* at 80° to give 0.60 g of the product (36% over-all yield, based on **1**). Recrystallization from water yielded the analytical sample: mp 195–196°; λ_{max} ($\epsilon \times 10^{-3}$) in pH 1 304 (13.5), in MeOH 282 (17.6), in pH 11 291 (12.10); R_{Ad} 1.82.

Anal. Calcd for $C_{10}H_{12}N_4OS$: C, 50.82; H, 5.12; N, 23.71. Found: C, 50.82; H, 5.26; N, 23.62.

9-*p*-Nitrobenzyl-6-[2-(2-carboxyethylthio)]purine (5).—To a rapidly stirred suspension of 6-mercapto-9-*p*-nitrobenzylpurine[13] (1.0 g, 3.49 mmoles) and anhydrous potassium carbonate in 30 ml of anhydrous dimethylformamide (dried over 4 Å molecular sieves) was added dropwise 0.534 g (0.314 ml, 3.49 mmoles) of 2-bromopropanoic acid. The mixture was stirred 5 hr under anhydrous conditions at room temperature. The solvent was removed *in vacuo* at 40–50° and the oily brown residue triturated with 20–30 ml of water. The pH was adjusted to 2–3 with 6 *N* HCl and the solid filtered, washed with three 5-ml portions of water, and dried *in vacuo* at room temperature to yield 1.23 g (98%). Recrystallization from ethanol gave the pure product, melting at 165–168° dec when placed on the hot stage at 125°; in the infrared spectrum a C=O absorption appeared at 1720 cm^{-1}; ultraviolet exhibited λ_{max} ($\epsilon \times 10^{-3}$) in pH 1 290 (20.6), in MeOH 286 (22.7), in pH 11 292 (24.8); R_{Ad} was 1.58.

Anal. Calcd for $C_{15}H_{13}N_5O_4S$: C, 50.13; H, 3.64; N, 19.49. Found: C, 49.69; H, 3.90; N, 19.41.

9-*p*-Nitrobenzyl-6-[2-(3-oxobutylthio)purine] (6).—A solution of 9-*p*-nitrobenzyl-6-[2-(2-carboxyethylthio)]purine (**5**) (1.0 g, 2.79 mmoles) in acetic anhydride (40 ml) was refluxed for 15 hr under anhydrous conditions. The acetic anhydride was removed *in vacuo* and the resulting brown oil was extracted with four 60-ml portions of ether. The dried ether extract yielded 0.4 g (41%) of crude product, mp 150–153°. Recrystallization from ethanol gave yellow plates: mp 157–159° dec; λ_{max} ($\epsilon \times 10^{-3}$) in MeOH 284 (26.3); R_{Ad} 1.58.

Anal. Calcd for $C_{16}H_{15}N_5O_3S$: C, 53.76; H, 4.23; N, 19.59. Found: C, 53.99; H, 4.20; N, 19.61.

Dakin–West Reactions on Phenoxy- and Thiophenoxyacetic Acid.—A mixture of thiophenoxyacetic acid (3.0 g, 17.9 mmoles), 30 ml of acetic anhydride, and 30 ml of anhydrous 2,6-lutidine was refluxed for 12 hr. The acetic anhydride and lutidine were removed *in vacuo* and the thiophenoxyacetone was distilled at 144° at 15 mm (bath temperature 160°) to yield 0.6 g (21%). The ketone was converted into its phenylhydrazone, mp 82.5 (lit.[14] 82.5). A mixture melting point with an authentic sample showed no depression.

A similar procedure was used for phenoxyacetic acid except that pyridine was used as the base. The phenoxyacetone, bp 118–120° at 20 mm (lit.[15] 110–112° at 12 mm), was obtained in a yield of 17%: semicarbazone, mp 173–174° (lit.[16] mp 173°).

Registry No.—**1**, 15268-84-5; **2**, 15260-05-6; **3**, 15260-06-7; **4**, 15260-07-8; **5**, 15260-08-9; **6**, 15260-09-0; thiophenoxyacetic acid, 103-04-8; phenoxyacetic acid, 122-59-8.

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Synthesis and Stereochemistry of Hydrophenanthrenes. VI. A Special Case of the Semmler–Wolff Rearrangement[1,2]

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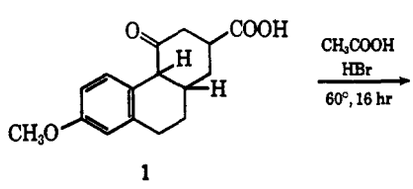
The aromatization of ring B in 1,2,3,4,4aβ,9,10,10aβ-octahydro-7-methoxy-4-oxo-2β-phenanthrenecarboxylic



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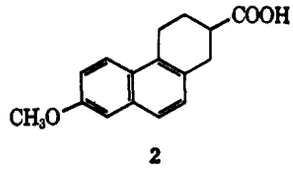

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(1) Part V: Z. G. Hajos, C. P. Parios, and M. W. Goldberg, *J. Org. Chem.*, **31**, 1360 (1966).

(2) All compounds described are racemates. As a matter of convenience only one enantiomeric series (10aβ hydrogen) has been pictured.

(3) Deceased Feb 17, 1964.